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Ionization-triggered Low Exciton Binding Energy in Covalent Organic Frameworks for Efficient Photocatalytic Synthesis of Benzimidazole

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1. General information

1.1 Chemicals

Unless otherwise stated, all the chemicals were purchased in analytical purity from commercial suppliers and used directly without further purification. 1,3,6,8-tetrakis(4-formylphenyl)pyrene was synthesized following the reported procedure[1].

1.2 Characterization methods

Powder X-ray diffraction (PXRD) patterns were collected on a Bruker D8 Advance diffractometer with Cu Kα radiation (2θ range: 2-40°; Scan step size: 0.02°; Time per step: 1 s). Liquid-state ^{1}H, ^{13}C, and ^{19}F NMR were recorded on Bruker Advance 600 MHz and 151 MHz spectrometers at 298 K, respectively. Chemical shifts (δ) are reported in ppm with residual solvent peak as the reference, and peaks are reported as follows: s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, with coupling constants in Hz. Fourier transform infrared (FT-IR) spectra were collected on a Nicolet 6700 spectrometer (Thermo Scientific, USA) equipped with an ATR cell. The specific Brunauer-Emmett-Teller (BET) surface area and pore size distribution were measured using a Micrometrics ASAP 2040 instrument at 77 K. High resolution transmission electron microscope (HRTEM) images were obtained on a Talos F200x instrument at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo ESCALAB 250XI spectrometer with non-monochromatic Al Kα x-rays as the excitation source and C 1s (284.6 eV) as the reference line. Solid-state diffuse reflectance Ultraviolet–visible spectroscopy (UV-vis) spectra were collected on a Shimadzu UV 3600

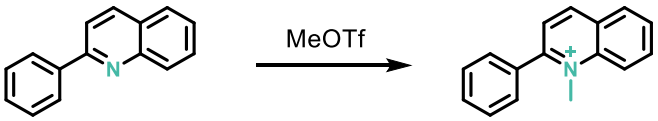
Spectrophotometer with $BaSO_4$ as the reference. Electron paramagnetic resonance (EPR) spectra were recorded on a Bruker GEMX nano spectrometer under visible light irradiation. Zeta potential was measured with a Malvern Zetasizer Nano ZS instrument. Temperature-dependent PL spectra from 80 K to 300 K were recorded on a Fluorolog-QM spectrophotometer (Horiba).

1.3 Electrochemical measurements

Electrochemical measurements were performed on the CHI 760E workstation (CH Instruments, China) with a standard three-electrode system, in which a platinum plate and a commercial Ag/AgCl electrode were used as the counter electrode and the reference electrode, respectively. The working electrode was prepared as follows: 15 mg of sample was thoroughly mixed with 200 μL isopropanol containing 5% Nafion, and the resulting suspension was carefully loaded on the ITO glass substrate (10 × 15 × 1.1 mm) and dried at 60 °C under vacuum for 1 h. 0.1 M Na_2SO_4 aqueous solution was employed as the electrolyte. For Mott-Schottky tests, the perturbation was set to be 5 mV with frequencies of 1000, 2000, and 3000 Hz.

2. Synthetic procedures

2.1 Model reaction



Scheme S1. Synthesis of 1-methyl-2-phenylquinolinium.

A 25 mL round-bottom flask was charged with 2-phenylquinoline (20.5 mg, 0.1 mmol), methyl triflate (MeOTf, 16.4 mg, 0.1 mmol), and dichloromethane (DCM, 2 mL). After being degassed with Ar for 10 min, the mixture was reacted at room

temperature for 12 h. After completing the reaction, the excess solvent was removed by rotary evaporation, and the concentrated residue was purified by flash chromatography on silica gel with PE/EA as the eluent to afford the product **1-methyl-2-phenylquinolinium** (27.0 mg, 0.073 mmol, 73%). ^{1}H NMR (DMSO-D_6, 600 MHz) δ 9.28 (d, J = 8.7 Hz, 1H), 8.63 (d, J = 8.76Hz, 1H), 8.52 (d, J = 8.28Hz, 1H), 8.34 (t, J = 8.7Hz, 1H), 8.17 (d, J = 7.26Hz, 1H), 8.10 (t, J = 7.44Hz, 1H), 7.75-7.73 (m, 2H), 7.81-7.80 (m, 3H), 4.38 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.1, 135.4, 135.2, 131.7, 130.9, 130.3, 127.7, 126.4, 126.1, 125.8, 122.9, 122.4, 119.7, 117.7, 114.9, 55.4.

2.2. Synthesis of NQ-COF$_{D4}$

A Pyrex glass tube (10 mL) was charged with 1,3,6,8-tetrakis(4-formylphenyl)pyrene (TFPPy, 30.9 mg, 0.05 mmol), benzidine (BZ, 18.4 mg, 0.1 mmol), vinylene carbonate (38.7 mg, 0.45 mmol), acetic acid (HOAc, 0.05 mL), $MgSO_4$ (72 mg), mesitylene (0.5 mL), and 1,4-dioxane (1.0 mL). Subsequently, the tube was sonicated for 10 minutes, degassed by three freeze-pump-thaw cycles (liquid nitrogen), and sealed under vacuum. After being heated in an oven at 120 ℃ for 3 days, the cooled suspension was centrifuged to separate the solid, which was repeatedly washed by THF and water until the solvent was colorless. **NQ-COF$_{D4}$** was finally obtained as a brown powder (39 mg, 97 %) after being dried under vacuum at 80 ℃.

2.3. Synthesis of NQ-COF$_{D4}$-Me

To synthesize the **NQ-COF$_{D4}$-Me,** a 50 mL round-bottom flask was charged with the corresponding **NQ-COF$_{D4}$** (31.5 mg), MeOTf (8.2 mg, 0.05 mmol), and DCM (10 mL). After being degassed with Ar for 10 min, the mixture was reacted at room

temperature for 12 h. The solid was separated by filtration under reduced pressure, and washed with DCM, CH_3OH, distilled water, and tetrahydrofuran (THF) successively. Finally, **NQ-COF$_{D4}$-Me** (32 mg) was obtained as a dark brown powder after being dried under vacuum at 80 ℃.

3. Characterization

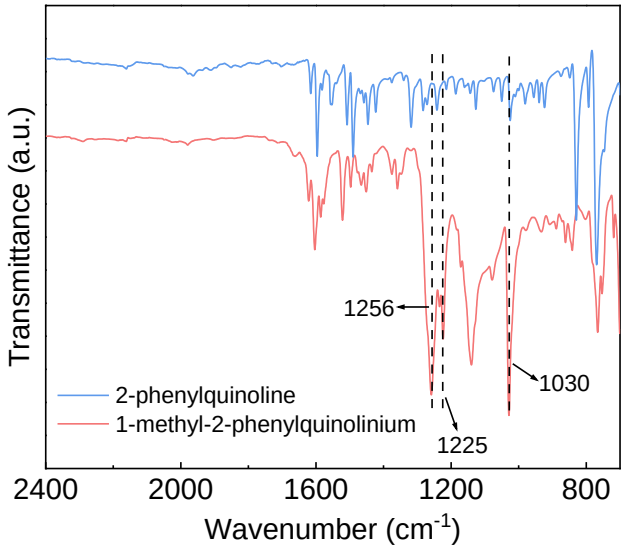


Figure S1. FT-IR spectra of 2-phenylquinoline and 1-methyl-2-phenylquinolinium.

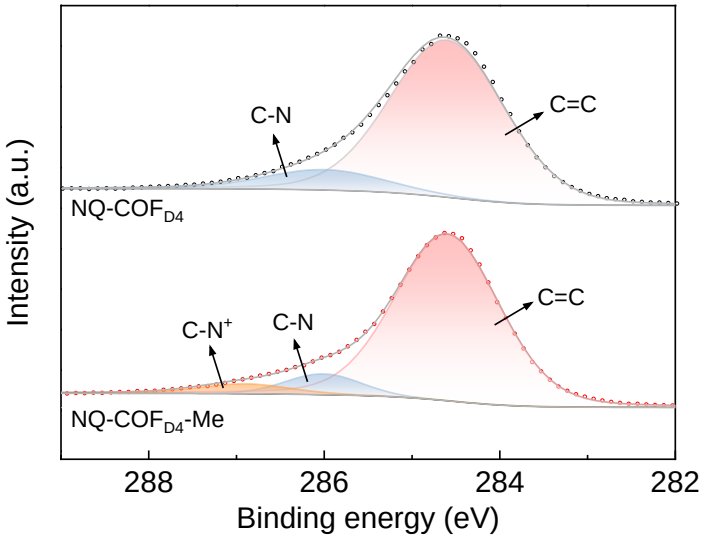


Figure S2. High resolution C 1s XPS spectra of NQ-COF$_{D4}$ and NQ-COF$_{D4}$-Me.

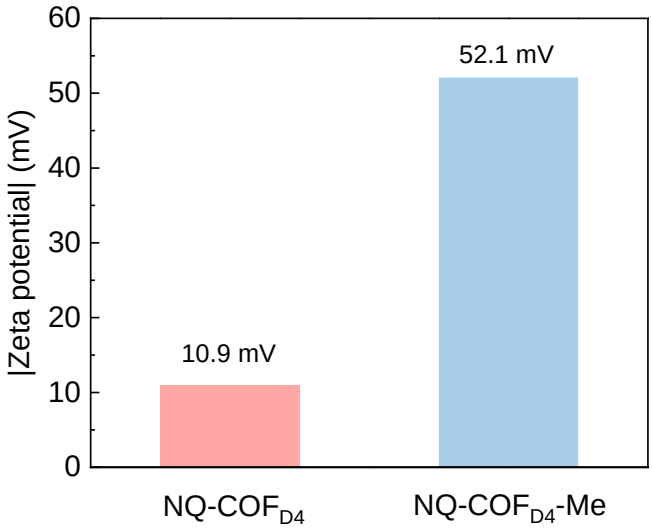


Figure S3. The absolute values of zeta potential of NQ-COF$_{D4}$ and NQ-COF$_{D4}$-Me.

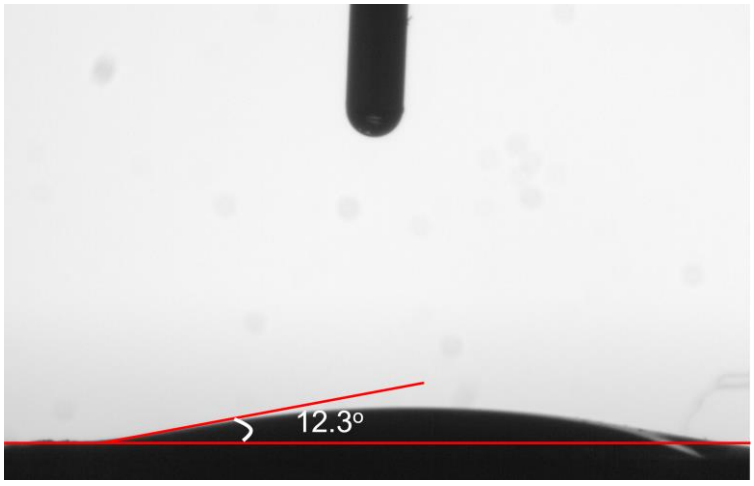


Figure S4. The water contact angle of NQ-COF$_{D4}$-Me.

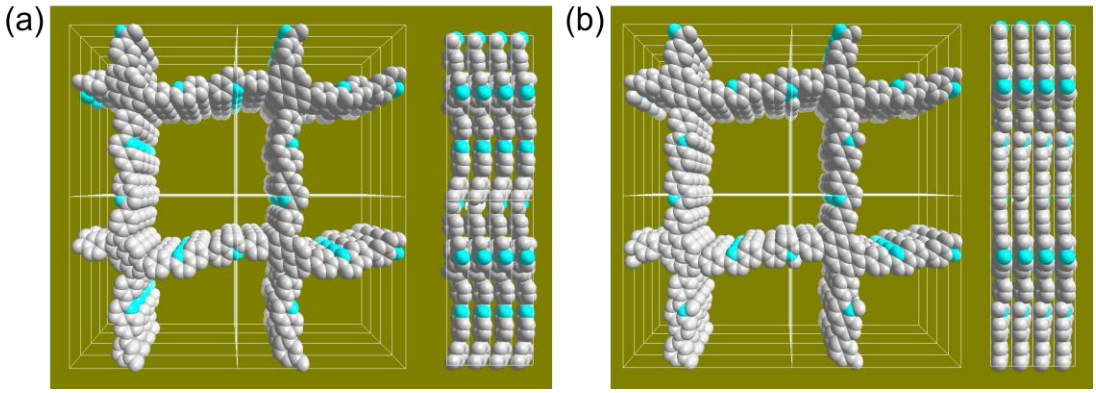


Figure S5. Top and side views of the simulated structure of (a) NQ-COF_{D4} and (b) NQ-COF_{D4}-Me with the eclipsed AA stacking model (light grey balls represent carbon atoms, blue balls represent nitrogen atoms).

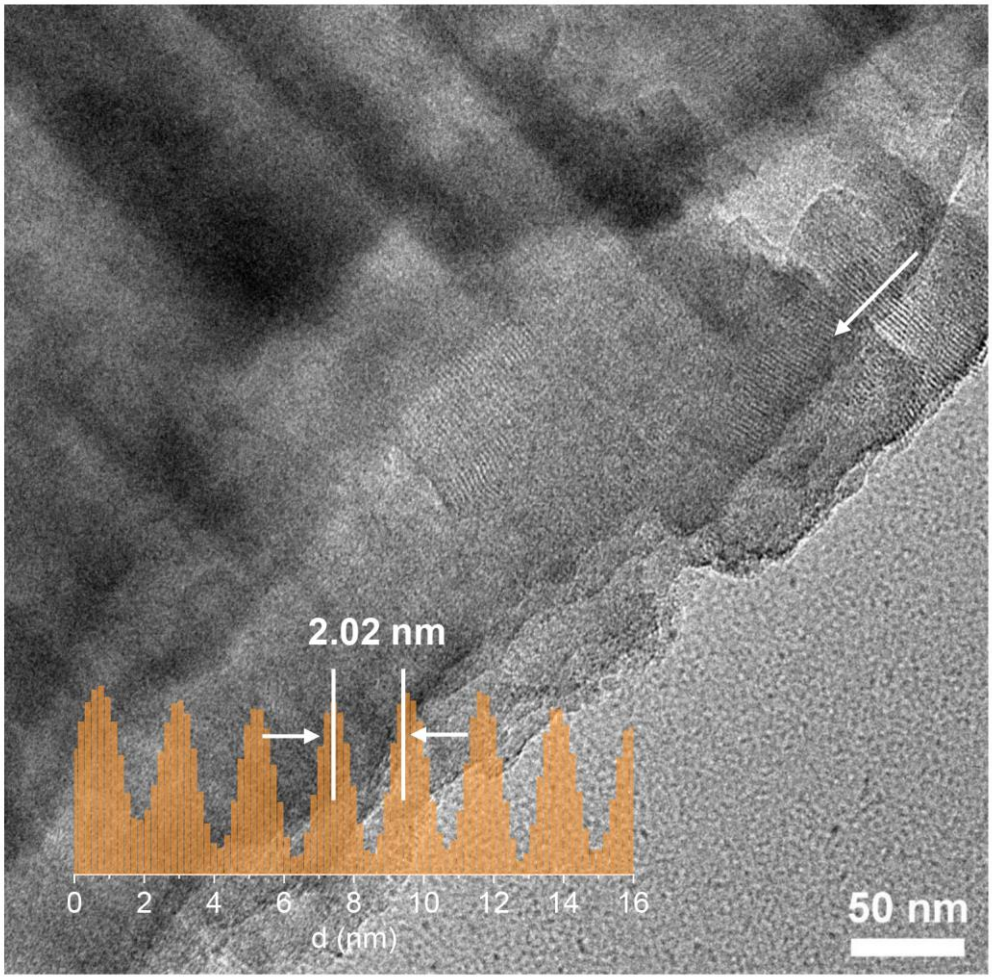


Figure S6. HRTEM image of NQ-COF_{D4}. The inset shows its corresponding line intensity profile along the direction marked by the white arrow.

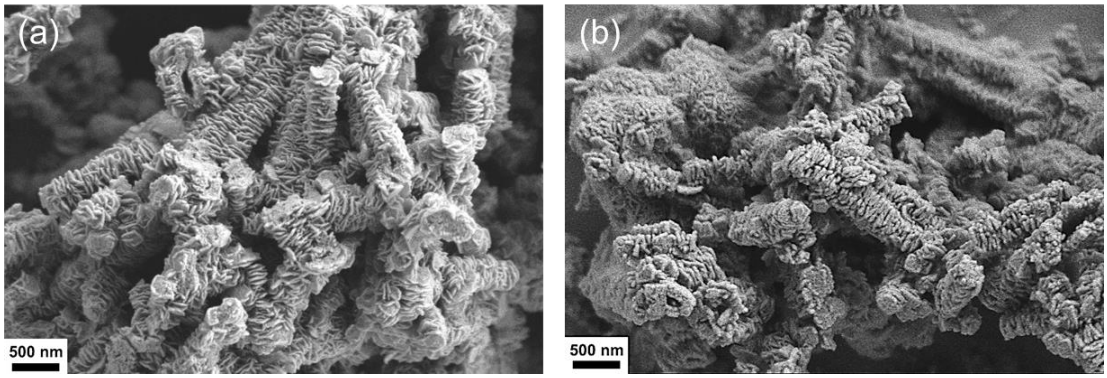


Figure S7. SEM images of NQ-COF$_{D4}$ and NQ-COF$_{D4}$-Me.

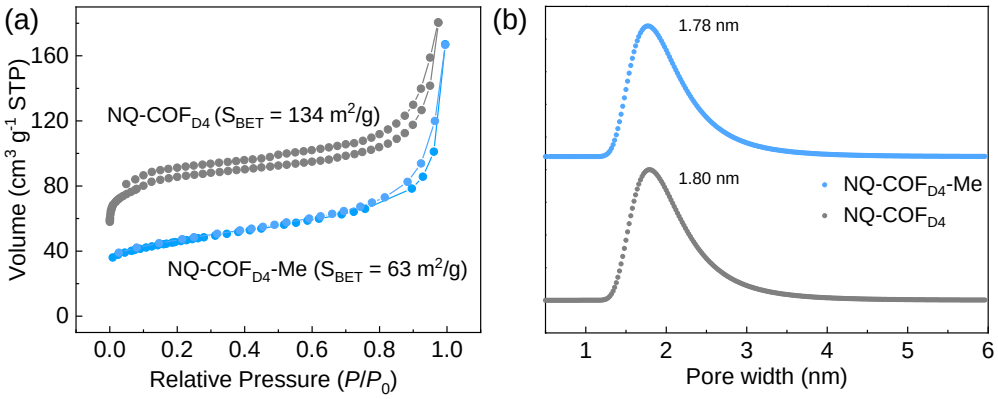


Figure S8. (a) N_2 adsorption/desorption isotherms of NQ-COF$_{D4}$ and NQ-COF$_{D4}$-Me. (b) Pore size distributions of NQ-COF$_{D4}$ and NQ-COF$_{D4}$-Me calculated from Dubinin-Radushkevitch model.

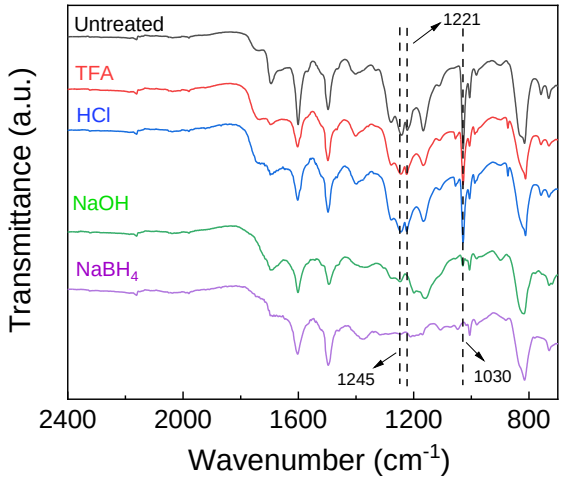


Figure S9. FT-IR spectra of NQ-COF$_{D4}$-Me before and after different chemical treatments.

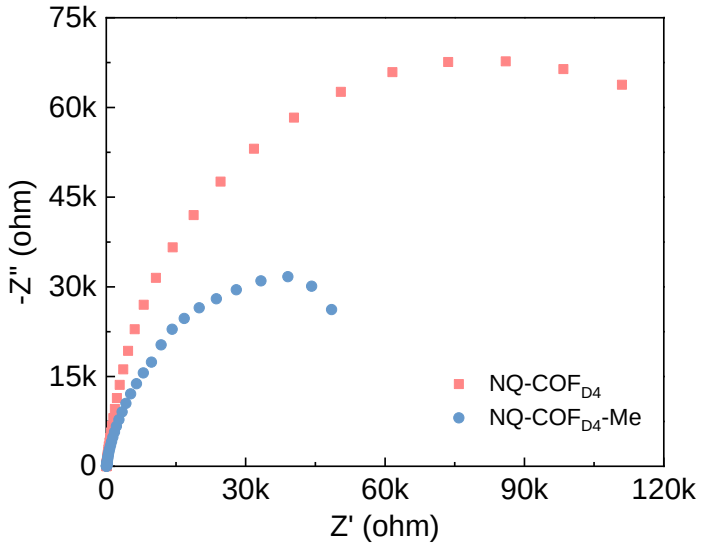


Figure S10. EIS spectra of NQ-COF$_{D4}$ and NQ-COF$_{D4}$-Me.

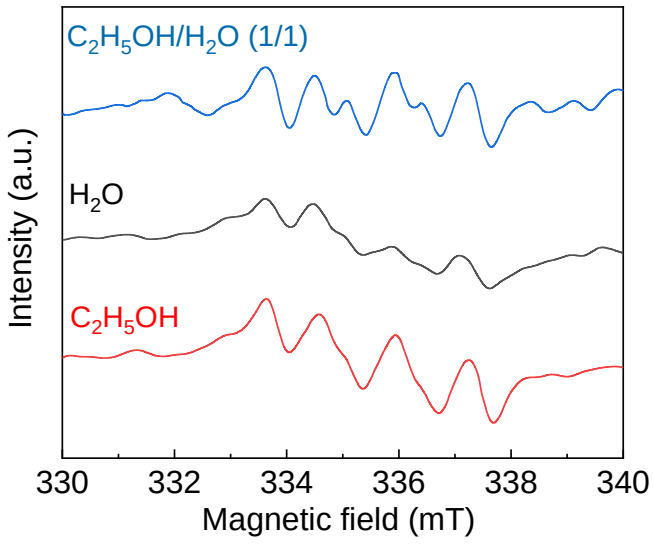


Figure S11. Detection of $\bullet O^{2-}$ signal in different solvents with NQ-COF$_{D4}$-Me as the photocatalyst.

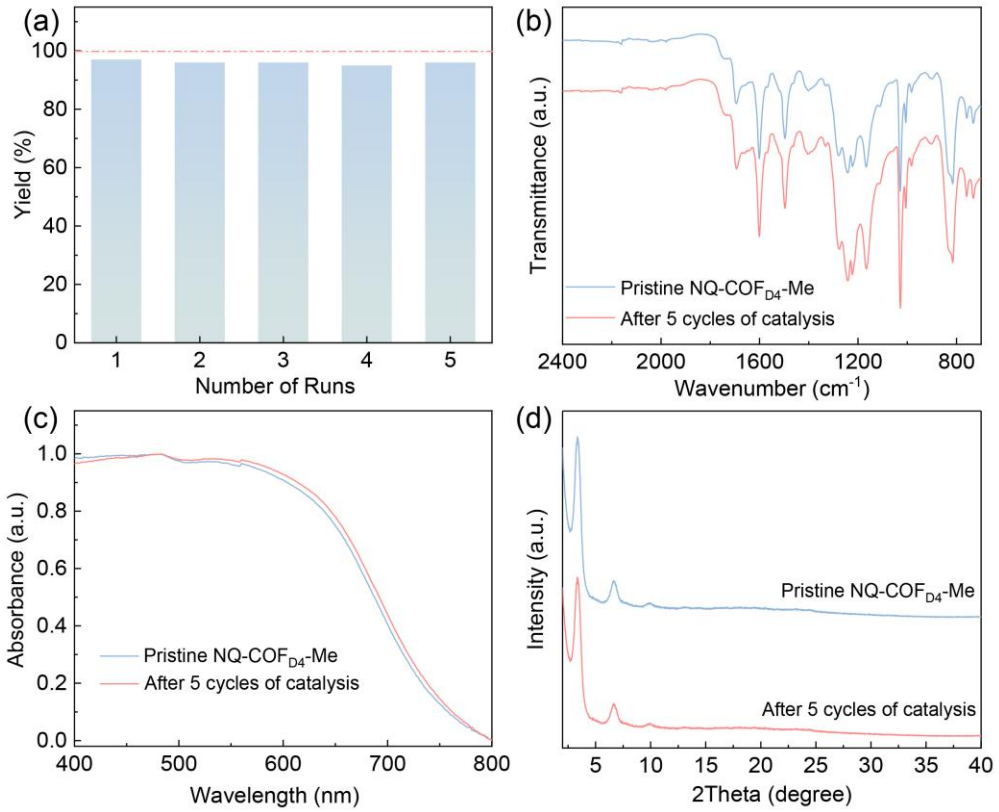


Figure S12. (a) Cycling stability of NQ-COF$_{D4}$-Me on the photocatalytic synthesis of **3a**. FT-IR spectra (b), UV-vis DRS spectra (c), and PXRD patterns (d) of NQ-COF$_{D4}$-Me before and after five cycles of photocatalysis.

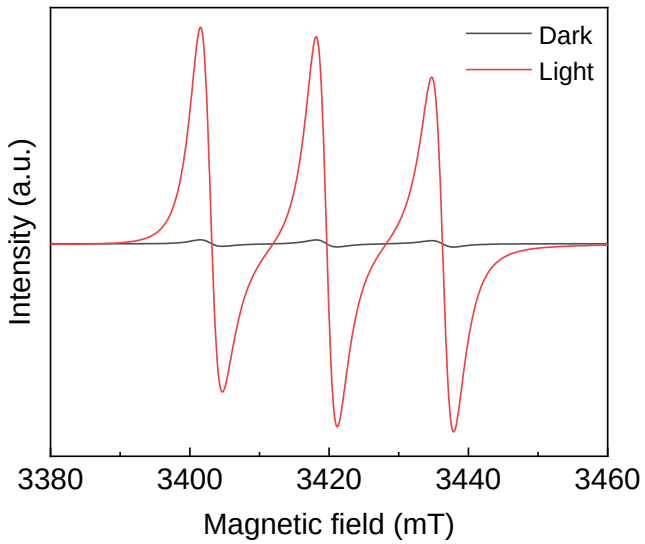


Figure S13. $^1O_2$ trapped by TEMP over NQ-COF$_{D4}$-Me in the dark and under light.

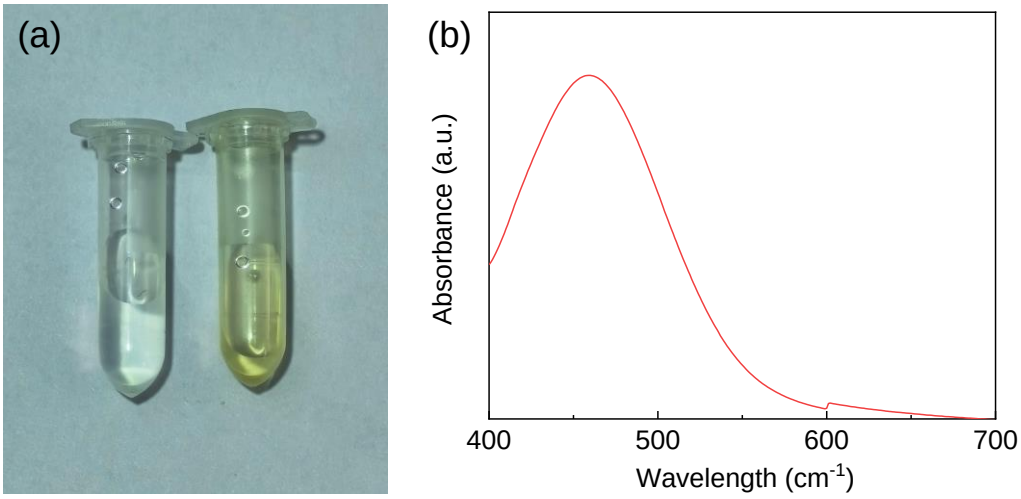


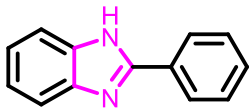
Figure S14. (a) Photo image of reaction solution with or without the chromogenic agent. (b) UV-vis absorption spectrum.

4. General procedure for photocatalytic benzimidazole synthesis

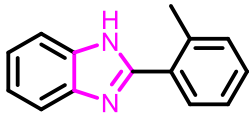
A 10 mL Schlenk tube equipped with a stir bar, was loaded with *o*-phenylenediamine (0.5 mmol), aldehyde (0.5 mmol), NQ-COF$_{D4}$-Me (5 mg), C_2H_5OH (1.0 mL), and H_2O (1.0 mL). Following evacuation and purging with O_2 for 10 minutes, the reaction mixture underwent irradiation in a photoreactor equipped with 18 W blue LEDs emitting light at 460-465 nm, along with a cooling fan, for a duration of 12 hours under an O_2 atmosphere. Upon completion of the reaction, the solid product was recovered by filtration, and the filtrate was concentrated under reduced pressure. The resulting residue was subjected to purification via flash chromatography on silica gel using a petroleum ether/ethyl acetate mixture as the eluent, leading to the isolation of the desired product.

Recycling test: The conversion of **3a** was selected as the model reaction to evaluate the stability of NQ-COF$_{D4}$-Me. After completing the reaction, NQ-COF$_{D4}$-Me was recovered by filtration, and washed repeatedly with distilled water and DCM. The

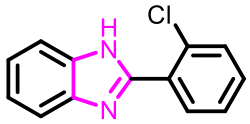
dried catalyst was directly used for the next run.



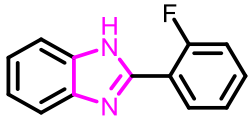
2-phenyl-1*H*-benzo[d]imidazole (3a): 93 mg, 0.48 mmol, 96 %. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.93 (br s, 1 H), 8.19 (d, *J* = 7.2 Hz, 2 H), 7.61 (s, 2 H), 7.57-7.54 (m, 2 H), 7.49 (t, *J* = 7.32, 1 H), 7.22-7.19 (m, 2 H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 151.7, 130.6, 130.4, 129.5, 126.9, 122.7.



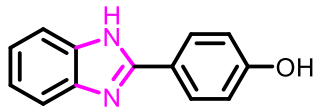
2-(o-tolyl)-1*H*-benzo[d]imidazole (3b): 99 mg, 0.48 mmol, 96 %. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.62 (br s, 1 H), 7.74 (d, *J* = 7.38 Hz, 1 H), 7.68 (d, *J* = 7.8 Hz, 1 H), 7.53 (d, *J* = 7.74 Hz, 1 H), 7.42-7.35 (m, 3 H), 7.24-7.18 (m, 2 H), 2.61 (s, 3 H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 152.4, 144.2, 137.5, 134.9, 131.7, 130.5, 129.9, 129.8, 126.4, 122.8, 121.9, 119.4, 117.7, 114.9, 111.7.



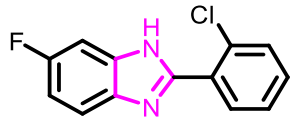
2-(2-chlorophenyl)-1*H*-benzo[d]imidazole (3c): 99 mg, 0.435 mmol, 87 %. ^{1}H NMR (600 MHz, DMSO-d_6) δ 13.04 (br s, 1 H), 8.20 (d, *J* = 8.64 Hz, 2 H), 7.67 (d, *J* = 7.8 Hz, 1 H), 7.64 (d, *J* = 8.7 Hz,2 H), 7.54 (d, *J* = 7.86 Hz, 1 H), 7.25-7.20 (m, 2 H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 150.6, 144.2, 135.5, 134.9, 129.6, 129.5, 128.6, 123.3, 122.3, 119.4, 111.9.



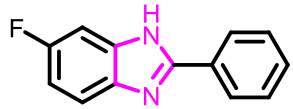
2-(2-fluorophenyl)-1*H*-benzo[d]imidazole (3d): 99 mg, 0.46 mmol, 94 %. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.61 (br s, 1 H), 8.25-8.22 (m, 1 H), 7.64 (s, 1 H), 7.59-7.55 (m, 1 H),7.46-7.39 (m, 2 H), 7.25-7.22 (m, 2 H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 160.8, 159.1, 146.8, 132.4, 132.3, 130.7, 125.6, 125.5, 117.1, 116.9; ^{19}F NMR (564 MHz, DMSO-d_6) δ -114.7.



4- (1*H*-benzo[d]imidazol-2-yl) phenol (3e): 93 mg, 0.445 mmol, 89 %. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.68 (br s, 1 H), 9.98 (s, 1 H), 8.00 (d, *J* = 8.7 Hz, 2 H), 7.54 (s, 2 H), 7.16 (s, 2 H), 6.92 (s, 2 H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 159.6, 152.2, 128.6, 122.1, 121.5, 116.1.

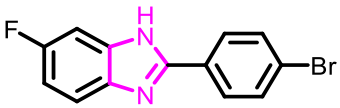


2-(2-chlorophenyl)-5-fluoro-*3*H-benzo[d]imidazole (3f): 113 mg, 0.46 mmol, 92 %. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.79 (br s, 1 H), 7.87-7.85 (m, 2 H), 7.63-7.32 (m, 5 H), 7.07 (s, 1 H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 151.3, 150.5, 140.3, 132.5, 132.4, 132.0, 131.9, 131.8, 130.9, 127.9, 120.6, 112.9, 111.5, 110.5, 105.0, 98.3; ^{19}F NMR (564 MHz, DMSO-d_6) δ -119.2, -121.3.

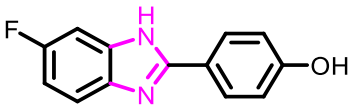


5-fluoro-2-phenyl-1*H*-benzo[d]imidazole (3g): 99 mg, 0.47 mmol, 94 %. ^{1}H NMR (600 MHz, DMSO-d_6) δ 13.07 (br s, 1 H), 8.16-8.15 (m, 2 H), 7.67-7.33 (m, 5 H), 7.07 (m, 1 H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 130.5, 130.3, 129.5, 126.9, 110.7, 110.3;

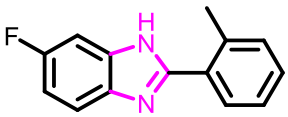
^{19}F NMR (564 MHz, DMSO-d_6) δ -119.6, -121.4.



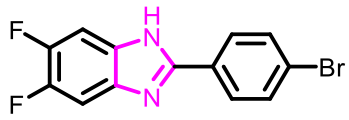
2-(4-bromophenyl)-5-fluoro-3*H*-benzo[d]imidazole (3h): 135 mg, 0.465 mmol, 93 %. ^{1}H NMR (600 MHz, DMSO-d_6) δ 13.19 (br s, 1 H), 8.13 (d, *J* = 8.52 Hz, 2 H), 7.81 (d, *J* = 8.46 Hz, 2 H), 7.63 (s, 1 H), 7.44 (s, 1 H), 7.12 (t, *J* = 8.67 Hz, 1 H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 160.0, 158.5, 152.1, 132.5, 129.5, 128.8, 123.9, 111.0, 110.9. ^{19}F NMR (564 MHz, DMSO-d_6) δ -119.2, -121.1.



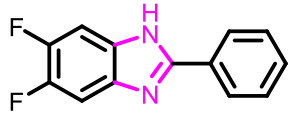
4-(5-fluoro-3*H*-benzo[d]imidazol-2-yl) phenol (3i): 107 mg, 0.47 mmol, 94 %. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.79 (br s, 1H), 10.00 (s, 1H), 7.98 (d, *J* = 8.4Hz, 2H), 7.58-7.26 (m, 2H), 7.00 (s, 1 H), 6.91 (d, *J* = 8.58 Hz, 2 H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 132.1, 128.7, 128.5, 121.4, 121.2, 116.2, 110.2, 109.8, 104.3; ^{19}F NMR (564 MHz, DMSO-d_6) δ -120.5, -121.9.



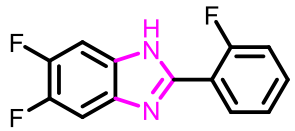
5-fluoro-2-(o-tolyl)-3*H*-benzo[d]imidazole (3j): 110 mg, 0.49 mmol, 98 %. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.77 (br s, 1 H),7.73 (d, *J* = 7.5 Hz, 1 H),7.53-7.48 (m ,1 H), 7.41-7.39 (d, *J* = 10.5 Hz, 2 H), 7.38 (d, *J* = 7.68 Hz, 1 H), 7.36-7.30 (m, 1 H), 7.12-7.04 (m, 1 H), 2.60 (s, 3 H) ; ^{13}C NMR (151 MHz, DMSO-d_6) δ 154.2, 144.4, 140.8, 137.4, 134.9, 131.6, 130.0, 129.8, 126.5, 120.2, 112.3, 110.0, 104.7, 98.1, 97.9, 21.5. ^{19}F NMR (564 MHz, DMSO-d_6) δ -120.5.



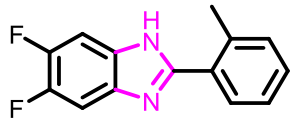
2-(4-bromophenyl)-5,6-difluoro-1*H*-benzo[d]imidazole (3k): 148 mg, 0.48 mmol, 96 %. ^{1}H NMR (600 MHz, DMSO-d_6) δ 13.46 (br s, 1 H), 8.11 (d, *J* = 8.52 Hz, 2 H), 7.78 (d, J = 8.52 Hz, 2 H), 7.73 (s, 1 H), 7.59 (s, 1 H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 152.5, 133.9, 133.5, 127.8, 118.9, 113.0. ^{19}F NMR (564 MHz, DMSO-d_6) δ -142.9, -144.8.



5,6-difluoro-2-phenyl-1*H*-benzo[d]imidazole (3l): 108 mg, 0.47 mmol, 94 %. ^{1}H NMR (600 MHz, DMSO-d_6) δ 13.22 (br s, 1 H), 8.15 (d, *J* = 7.26 Hz, 2 H), 7.64-7.49 (m, 5 H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 153.7, 148.1, 146.6, 139.6, 130.6, 130.1, 129.5, 126.9, 126.7; ^{19}F NMR (564 MHz, DMSO-d_6) δ -143.3, -145.0.

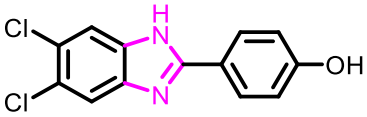


5,6-difluoro-2-(2-fluorophenyl)-1*H*-benzo[d]imidazole (3m): 112 mg, 0.455 mmol, 91 %. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.84 (s, 1 H),8.23-8.20 (m, 1 H),7.67-7.57 (m, 3 H),7.48-7.45 (m, 1 H), 7.42-7.39 (m, 1 H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 160.7, 159.0, 148.8, 132.7, 130.5, 125.6, 118.0, 117.9, 117.1, 116.9; ^{19}F NMR (564 MHz, DMSO-d_6) δ -114.7, -142.9, -144.7.

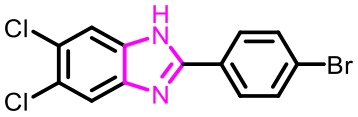


5,6-difluoro-2-(o-tolyl)-1*H*-benzo[d]imidazole (3n): 113 mg, 0.465 mmol, 93 %. ^{1}H

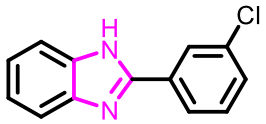
NMR (600 MHz, DMSO-d_6) δ 12.90 (br s,1 H), 7.72 (d, *J* = 8.34 Hz, 1 H), 7.65 (s, 2 H), 7.43-7.40 (m, 1 H), 7.39 (s, 1 H), 7.38-7.36 (s, 1 H), 2.59 (s, 3 H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 154.4, 148.0, 146.4, 137.5, 131.8, 130.1, 129.9, 129.8, 126.5, 21.4; ^{19}F NMR (564 MHz, DMSO-d_6) δ -143.5, -145.3.



4-(5,6-dichloro-1*H*-benzo[d]imidazol-2-yl) phenol (3o): 135 mg, 0.485 mmol, 97 %. ^{1}H NMR (600 MHz, DMSO-d_6) δ 13.01 (br s, 1 H), 10.09 (s, 1 H), 8.00 (s, 2 H), 7.85-7.57 (m, 2 H), 6.93 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 151.9, 134.2, 133.5, 127.5, 119.0, 112.6.



2-(4-bromophenyl)-5,6-dichloro-1*H*-benzo[d]imidazole (3p): 162 mg, 0.475 mmol, 95 %. ^{1}H NMR (600 MHz, DMSO-d_6) δ 13.31 (br s, 1 H), 8.11 (d, *J* = 8.58 Hz, 2 H), 7.87 (s, 2 H), 7.80 (d, *J* = 8.58 Hz, 2 H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 154.3, 131.1, 129.7, 129.6, 127.2.



(3-chlorophenyl)-1H-benzo[d]imidazole (3q):105 mg, 0.46 mmol, 92 %. ^{1}H NMR (600 MHz, DMSO-d6) δ 13.01 (br s, 1 H), 8.21 (br s, 1 H), 8.13 (br s, 1 H), 7.61-7.54 (m, 4 H), 7.22 (br s, 2 H); ^{13}C NMR (151 MHz, DMSO-d6) δ 150.2, 134.2, 132.9, 132.7, 131.4, 130.0, 129.4, 126.5, 125.8, 125.5, 123.1.

Table S1. Comparison of photocatalytic activities of the reported COFs, POPs, and MOFs for benzimidazole synthesis.

Photocatalyst	Reaction conditions	Yield (%) of 3a	Reference
BTT-TPA-COF	dosage (0.5 mg), C_2H_5OH and 36 W blue LED under O_2 atmosphere at rt, 7 h	85	2
NQ-COF_{A1}-OPR	dosage (5 mg), H_2O/C_2H_5OH, and 18 W blue LED under O_2 atmosphere at rt, 12 h	97	3
BO-COF_{F3}	dosage (5 mg), H_2O/C_2H_5OH, and 18 W blue LED under O_2 atmosphere at rt, 12 h	95	4
TPT-COF	dosage (15 mg), C_2H_5OH, and 40 W blue LED under air atmosphere at rt, 6 h	80	5
TZ-HCP1D	dosage (10 mg), C_2H_5OH, and 6 W white LED under air atmosphere at rt, 1 h	99	6
Ru-POP	dosage (3 mg), C_2H_5OH, and 24 W fluorescent bulb under air atmosphere at rt, 2 h	99	7
CuO@Ag/NH_2-MIL-88B	dosage (30 mg), C_2H_5OH, and 100 W LED under air atmosphere at 55 ^oC, 3 h	96	8
I_2@Cd-MOF	DMSO and under air atmosphere at rt, 6 h	85	9
NQ-COF_{D4}-Me	dosage (5 mg), H_2O/C_2H_5OH, and 18 W blue LED under O_2 atmosphere at rt, 12 h	97	This work

5. Copies of NMR and HRMS spectra

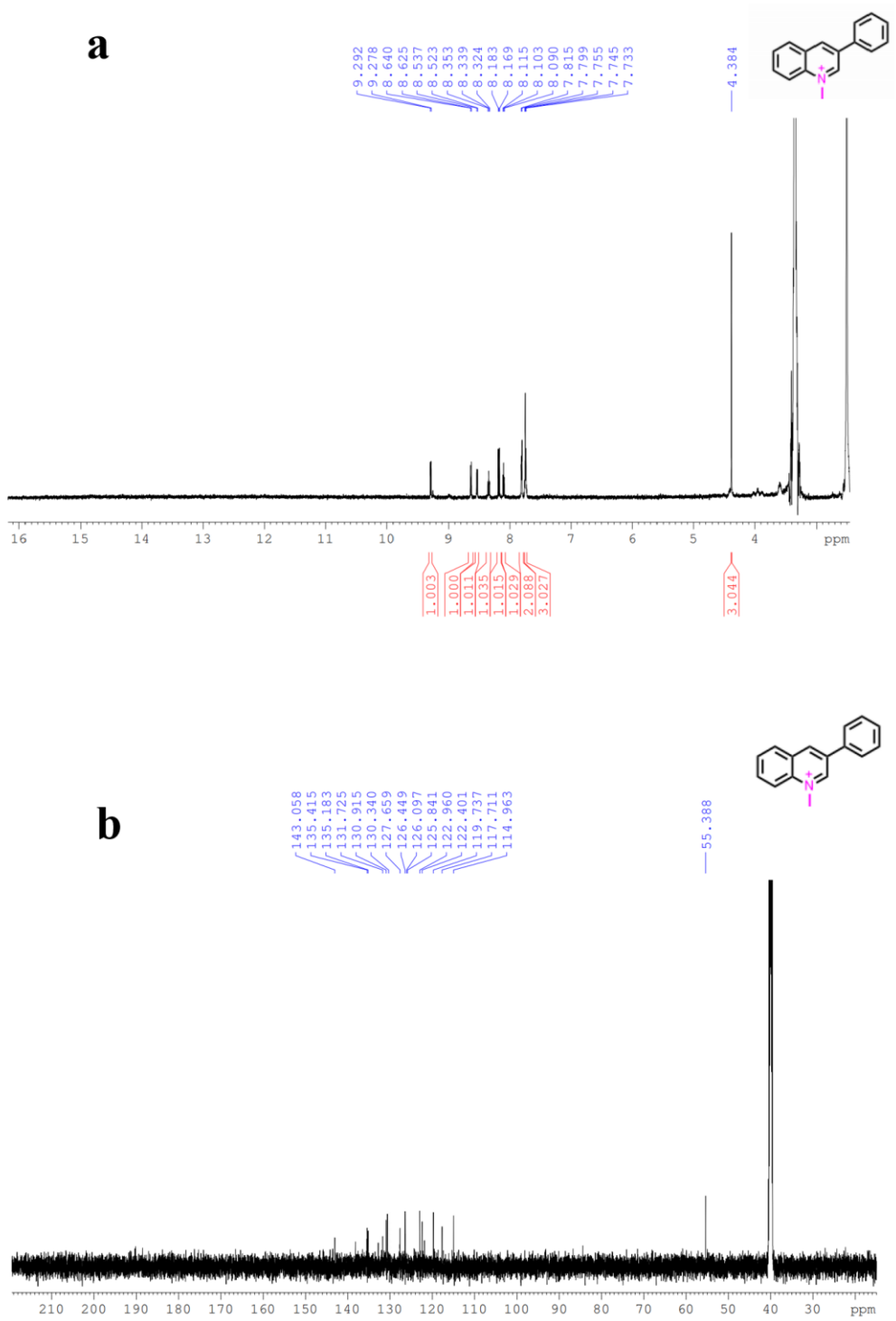


Figure S15. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of **1-methyl-2-phenylquinolinium**.

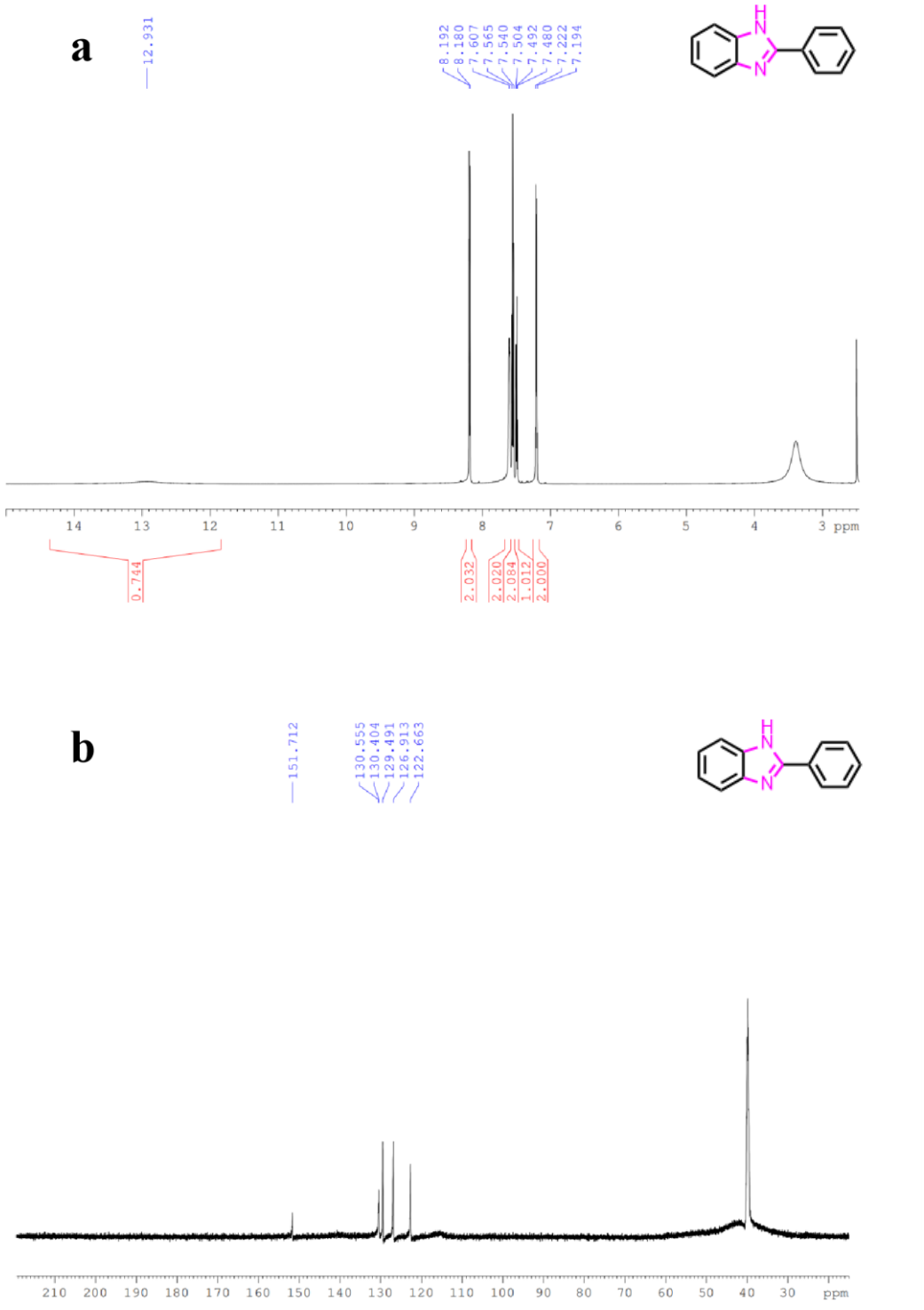


Figure S16. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of **3a**.

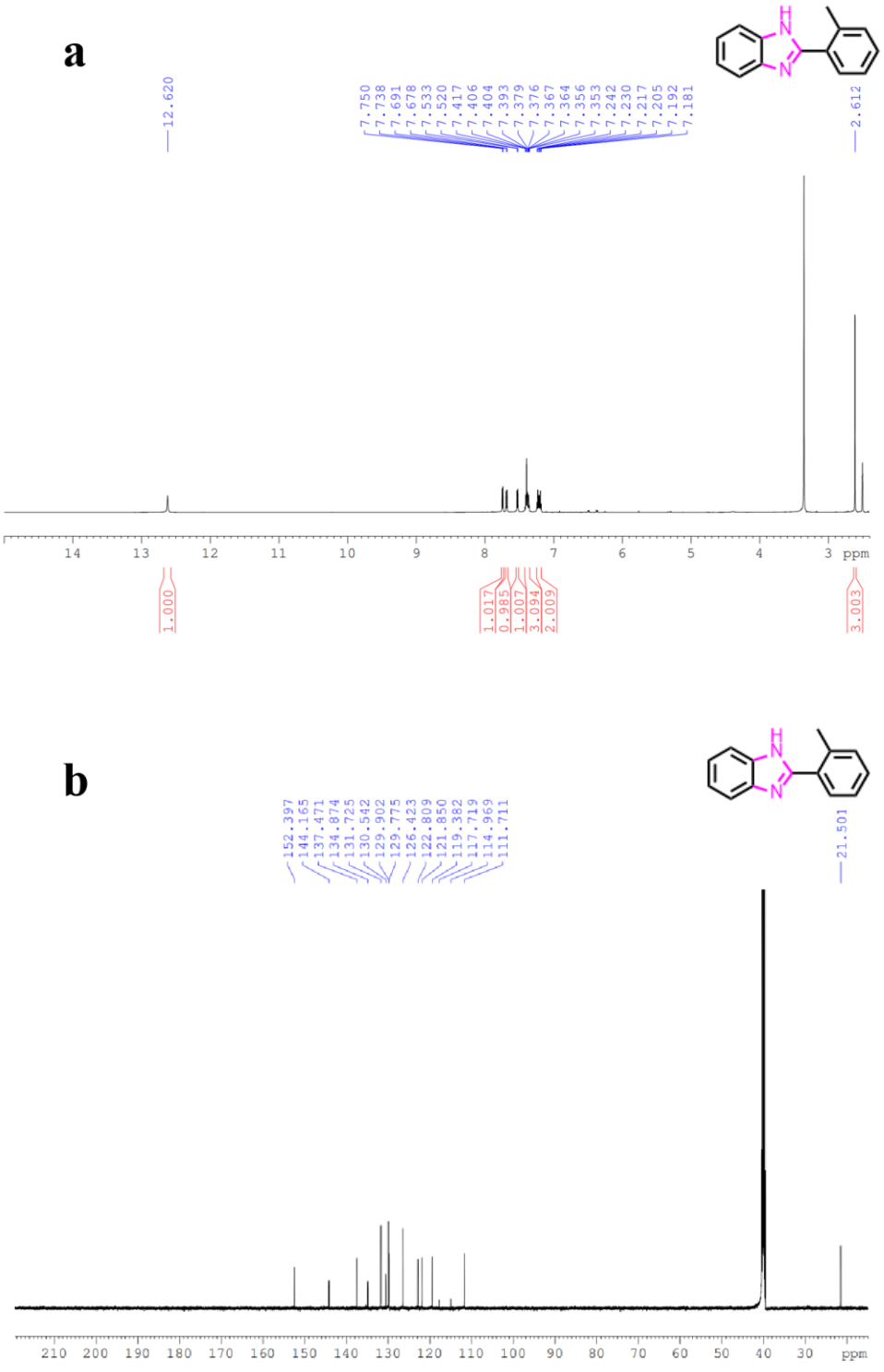


Figure S17. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of **3b**.

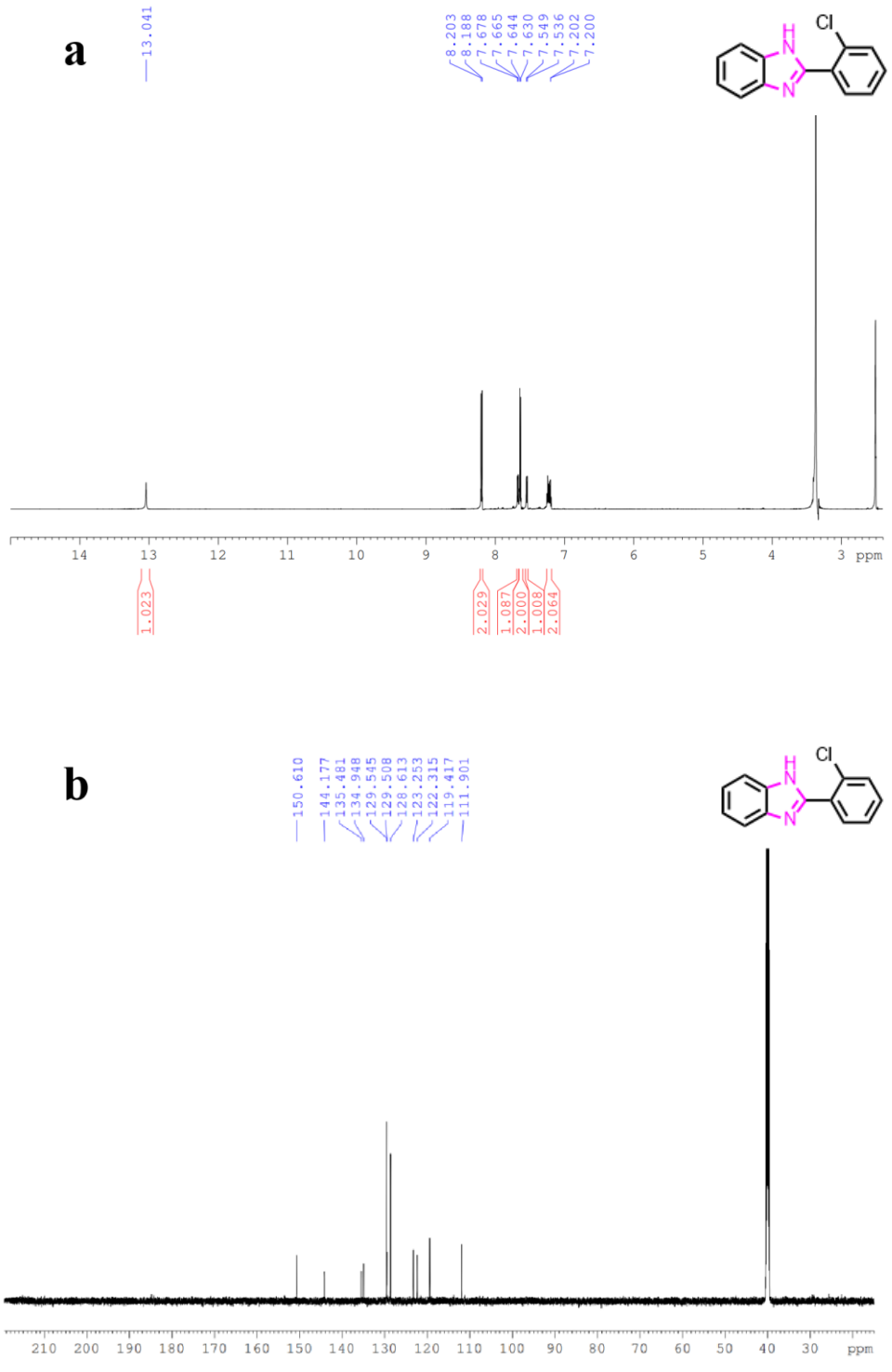
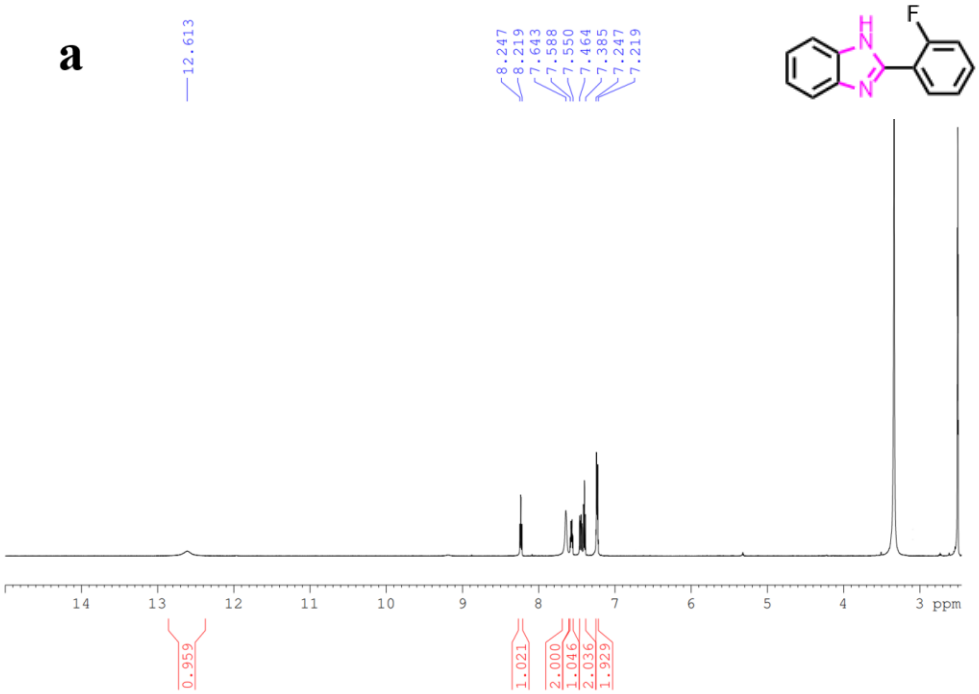
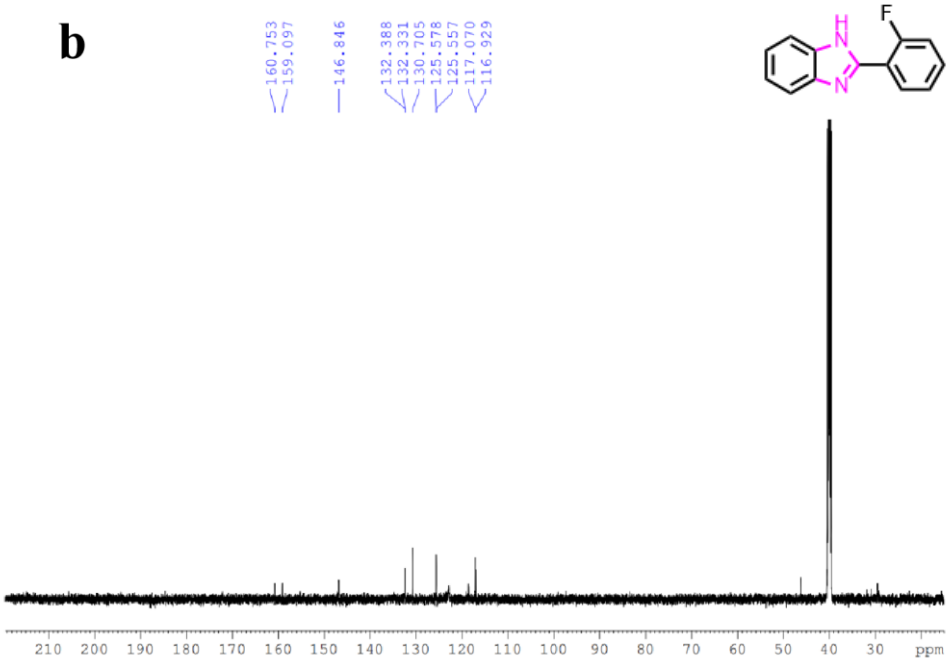


Figure S18. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of **3c**.


a
12.613
8.247
8.219
7.643
7.588
7.550
7.464
7.385
7.247
7.219
F
14 13 12 11 10 9 8 7 6 5 4 3 ppm
0.959
1.021
2.000
1.046
2.036
1.929


b
160.753
159.097
146.846
132.388
132.331
130.705
125.578
125.557
117.070
116.929
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm

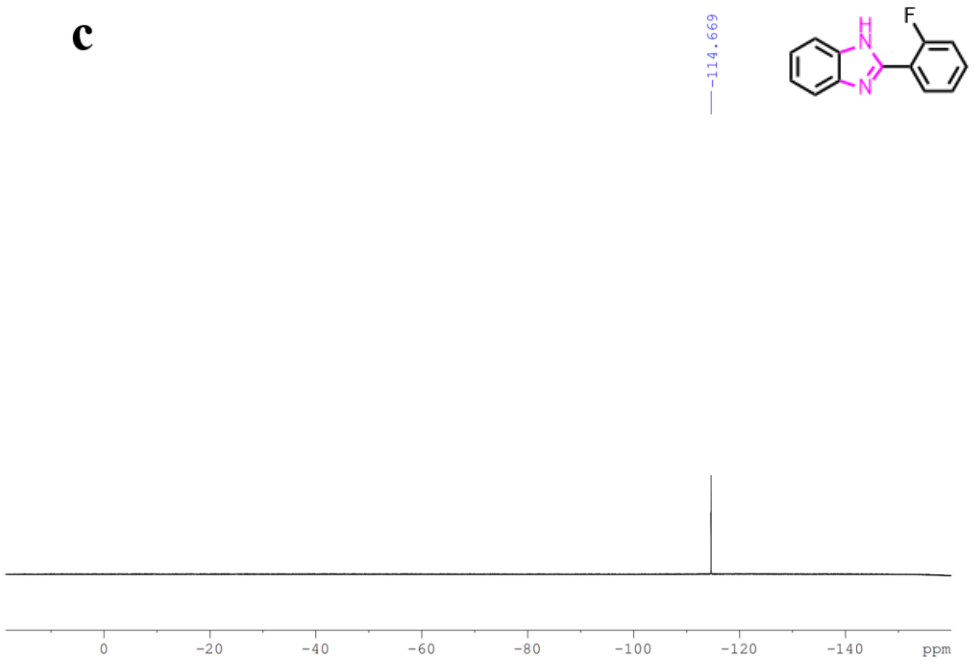
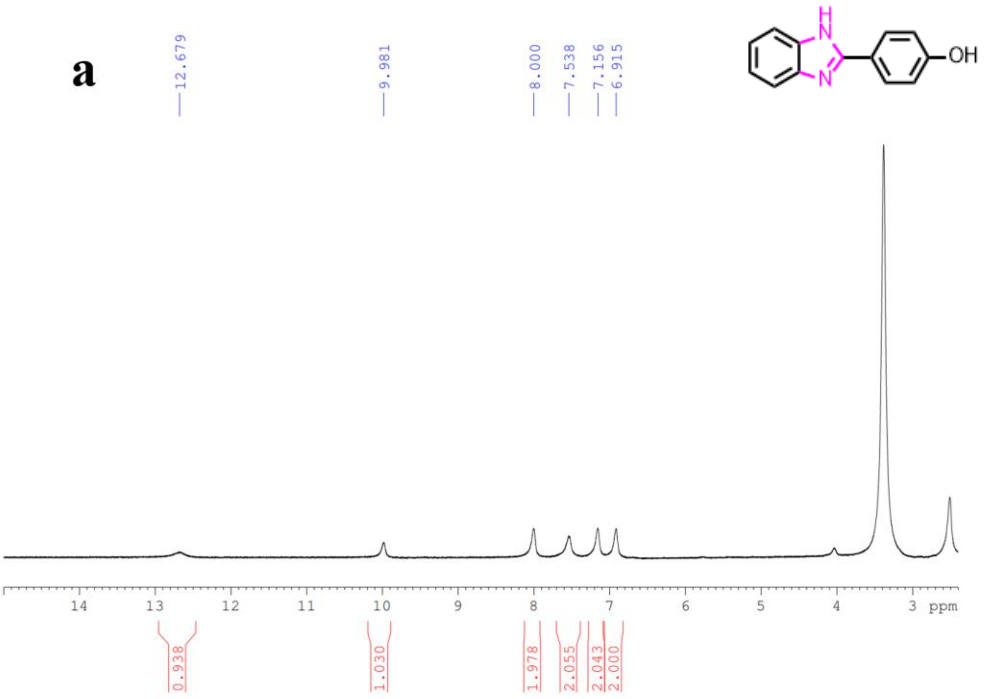


Figure S19. (a) ^{1}H NMR, (b) ^{13}C NMR, and (c) ^{19}F NMR spectra of **3d**.



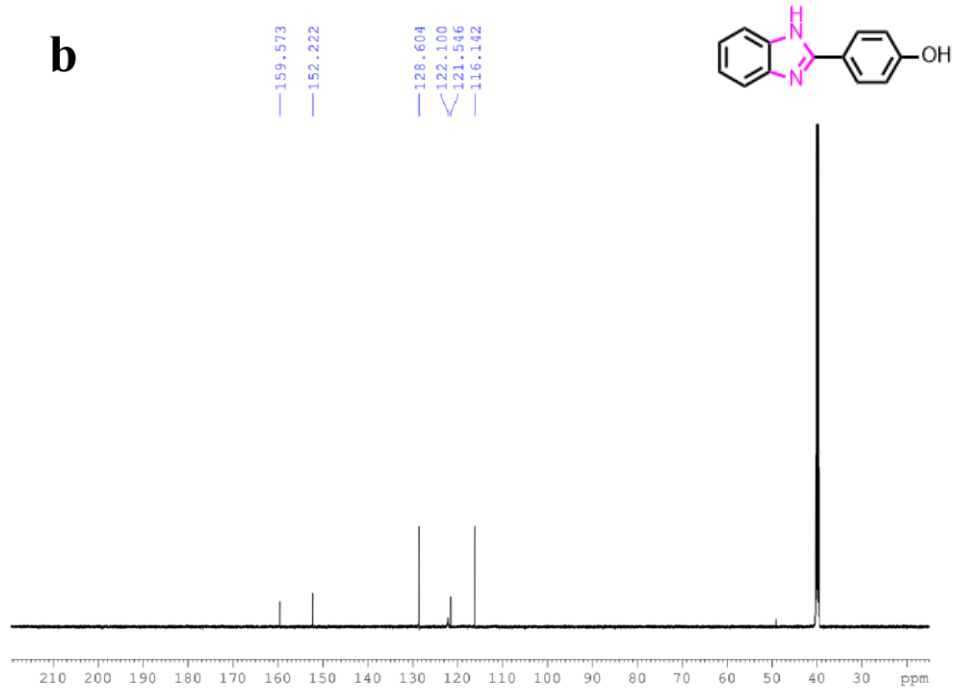
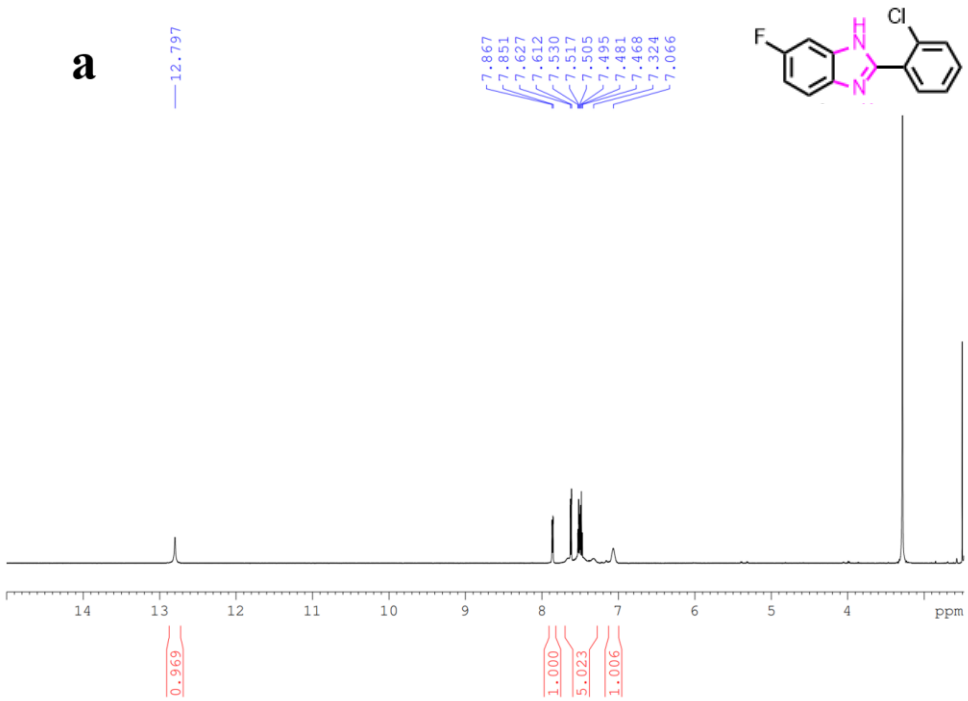


Figure S20. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of **3e**.



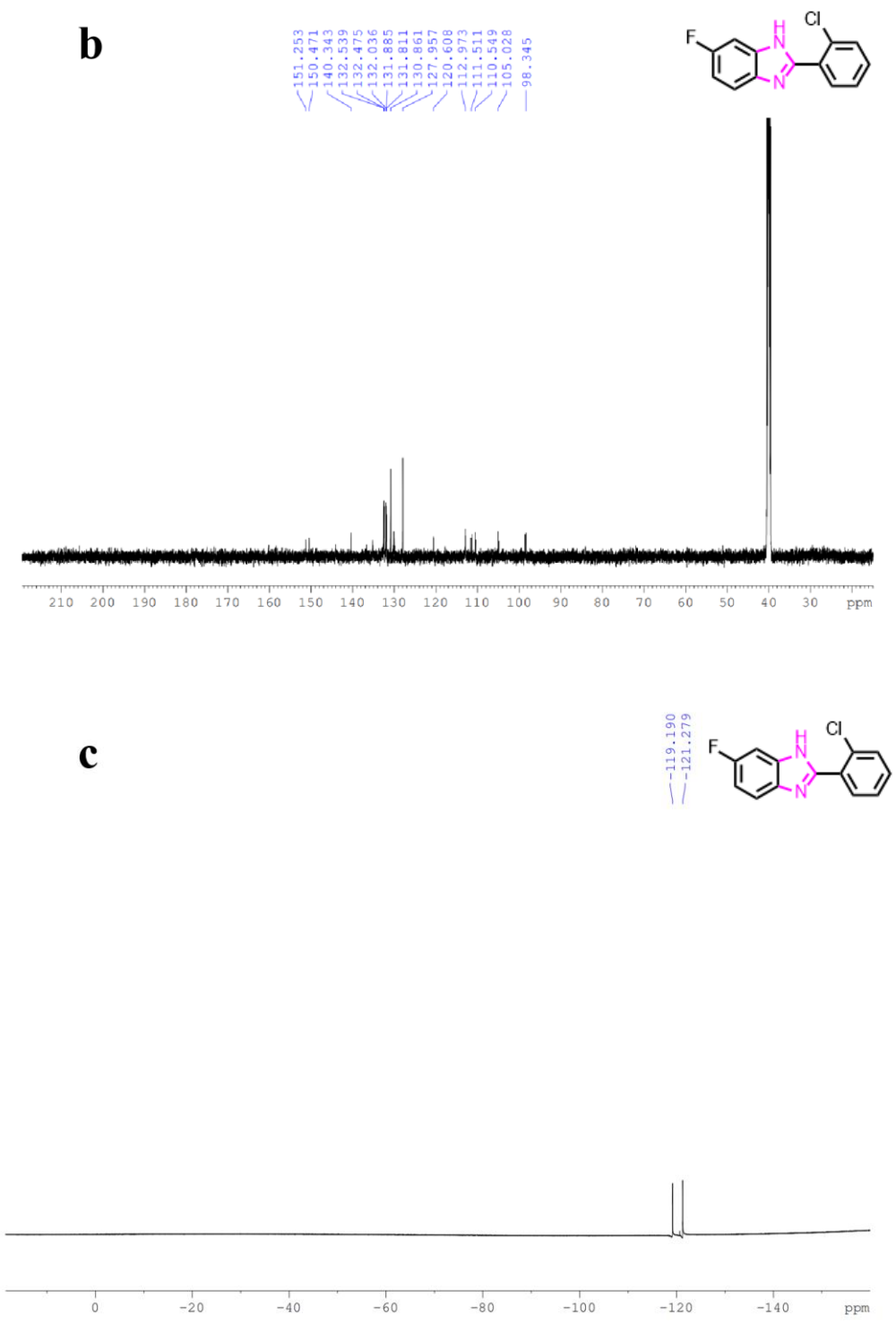
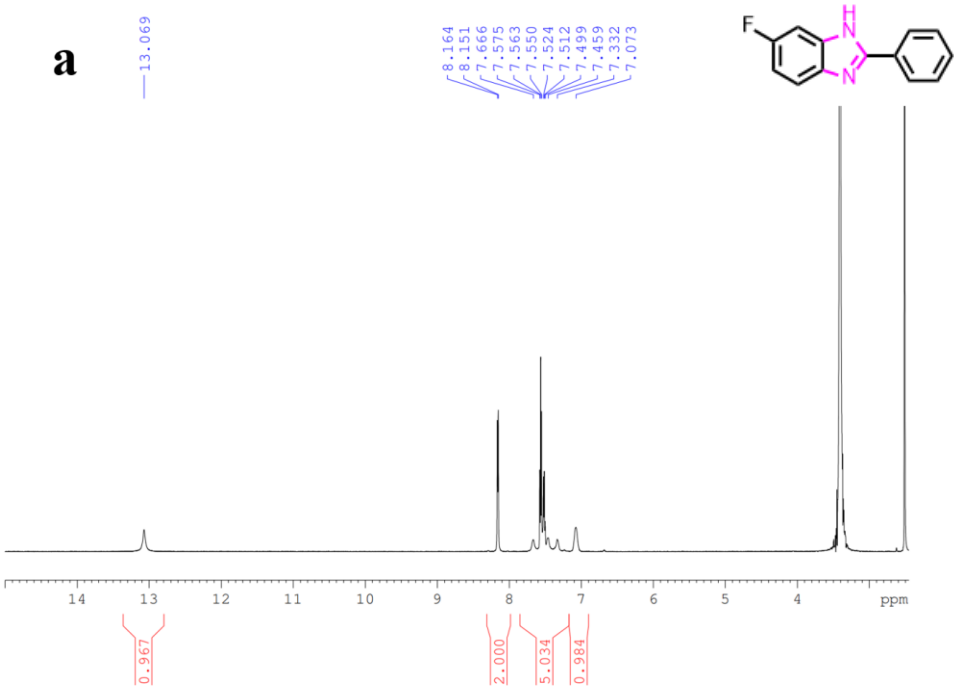


Figure S21. (a) ^{1}H NMR, (b) ^{13}C NMR, and (c) ^{19}F NMR spectra of **3f**.


a
13.069
8.164
8.151
7.666
7.575
7.563
7.550
7.524
7.512
7.499
7.459
7.332
7.073
F
H
N
N
14
13
12
11
10
9
8
7
6
5
4
ppm
0.967
2.000
5.034
0.984

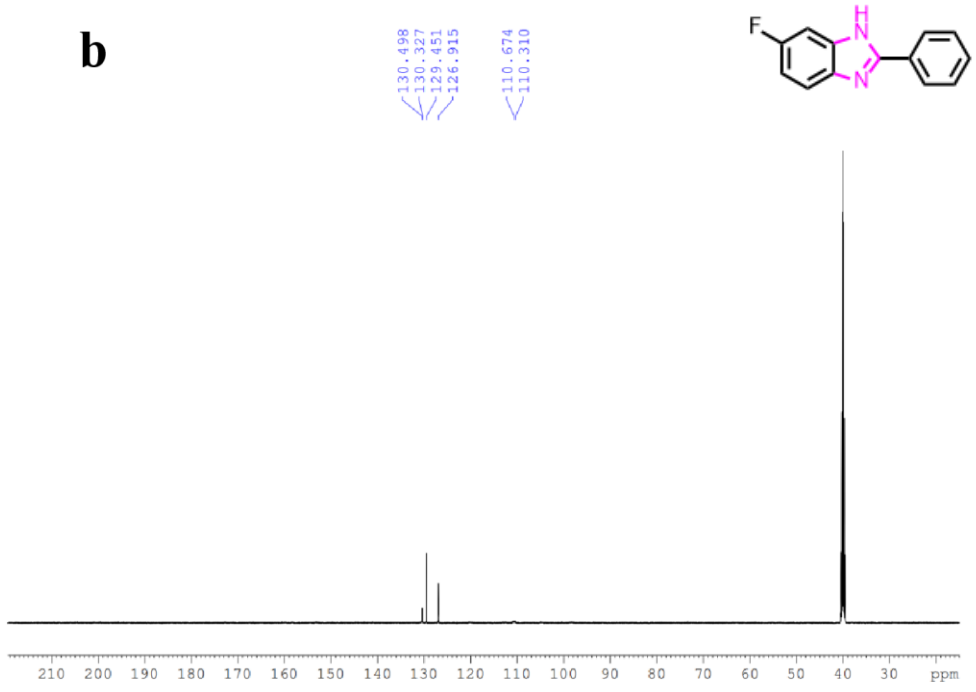
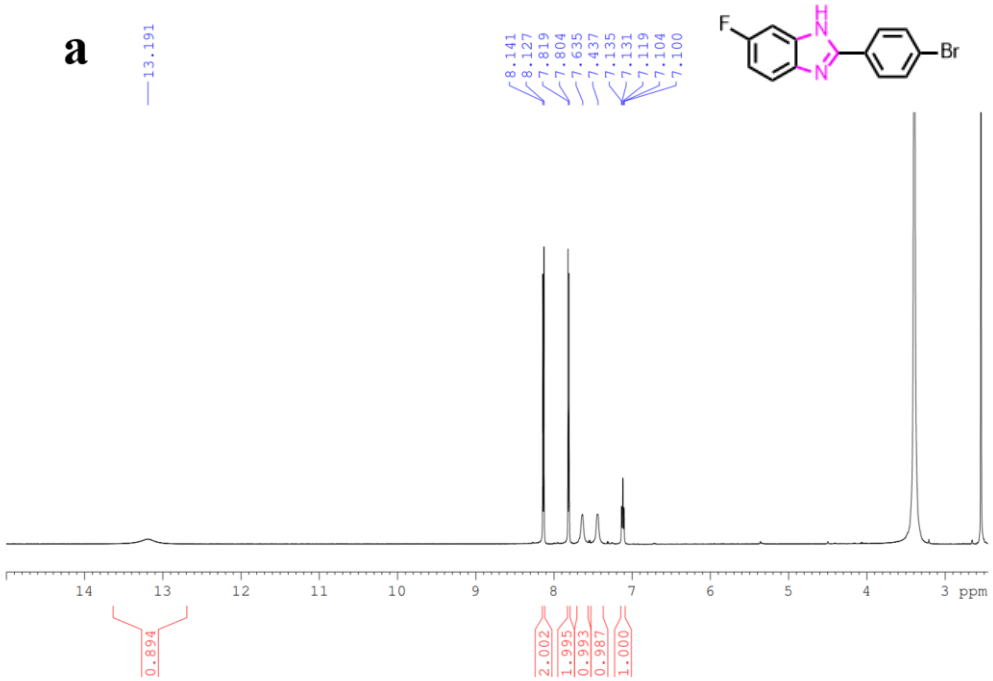

b
130.498
130.327
129.451
126.915
110.674
110.310
F
H
N
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

Figure S22. (a) ^{1}H NMR, (b) ^{13}C NMR, and (c) ^{19}F NMR spectra of **3g**.



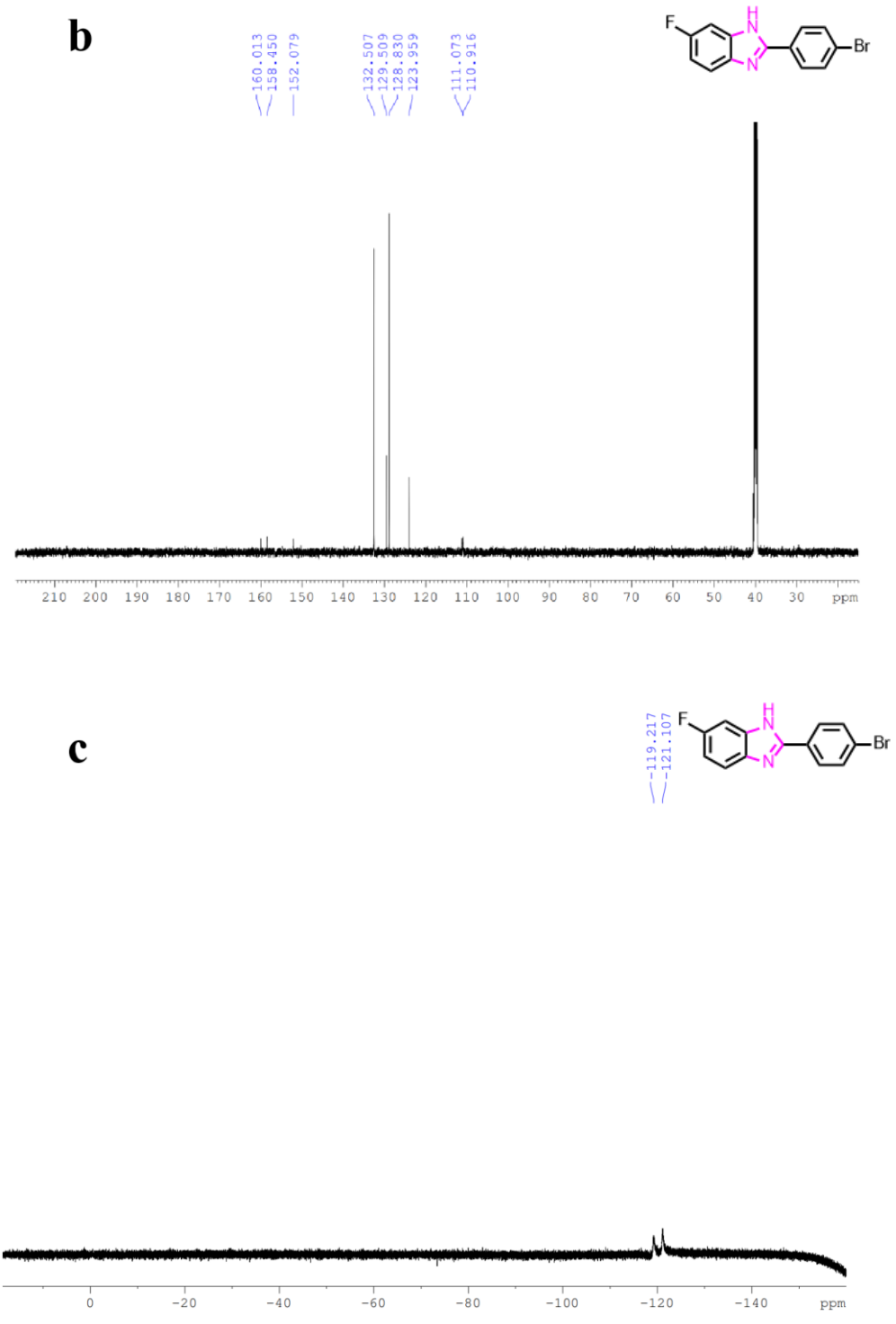
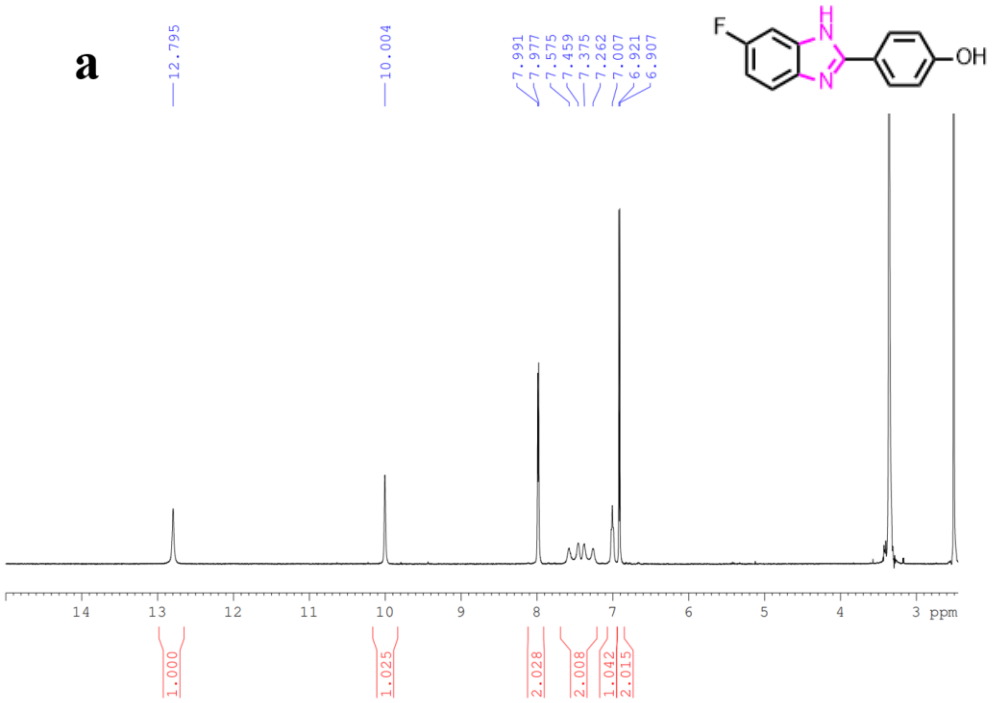
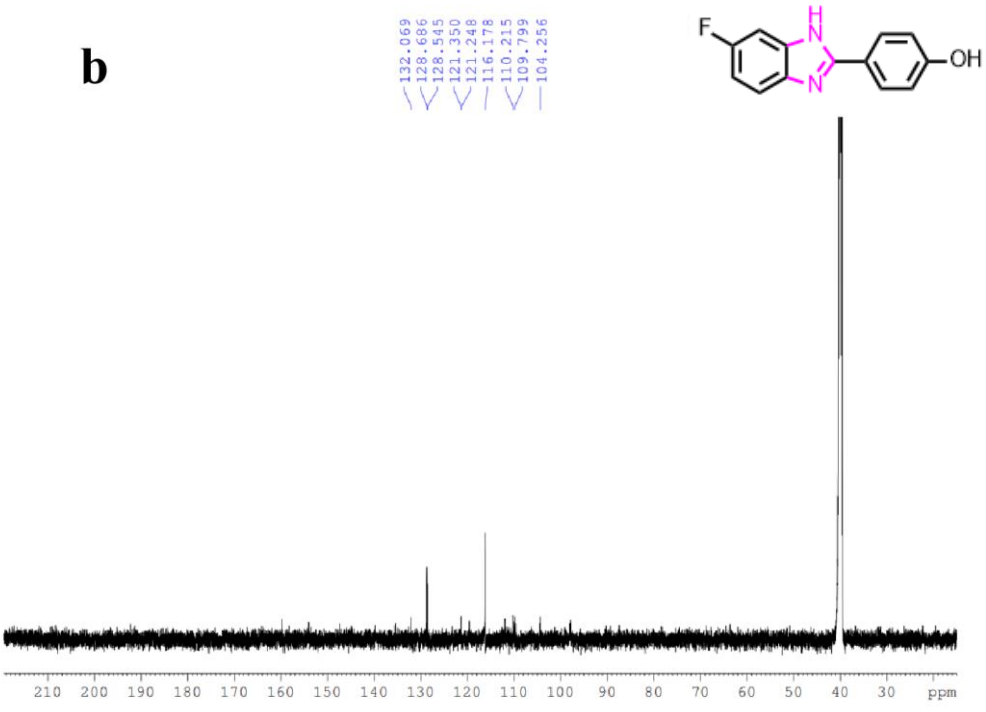


Figure S23. (a) ^{1}H NMR, (b) ^{13}C NMR, and (c) ^{19}F NMR spectra of **3h**.


a
12.795
10.004
7.991
7.977
7.575
7.459
7.375
7.262
7.007
6.921
6.907
F
N
H
N
OH
14
13
12
11
10
9
8
7
6
5
4
3 ppm
1.000
1.025
2.028
2.008
1.042
2.015


b
132.069
128.686
128.545
121.350
121.248
116.178
110.215
109.799
104.256
F
N
H
N
OH
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

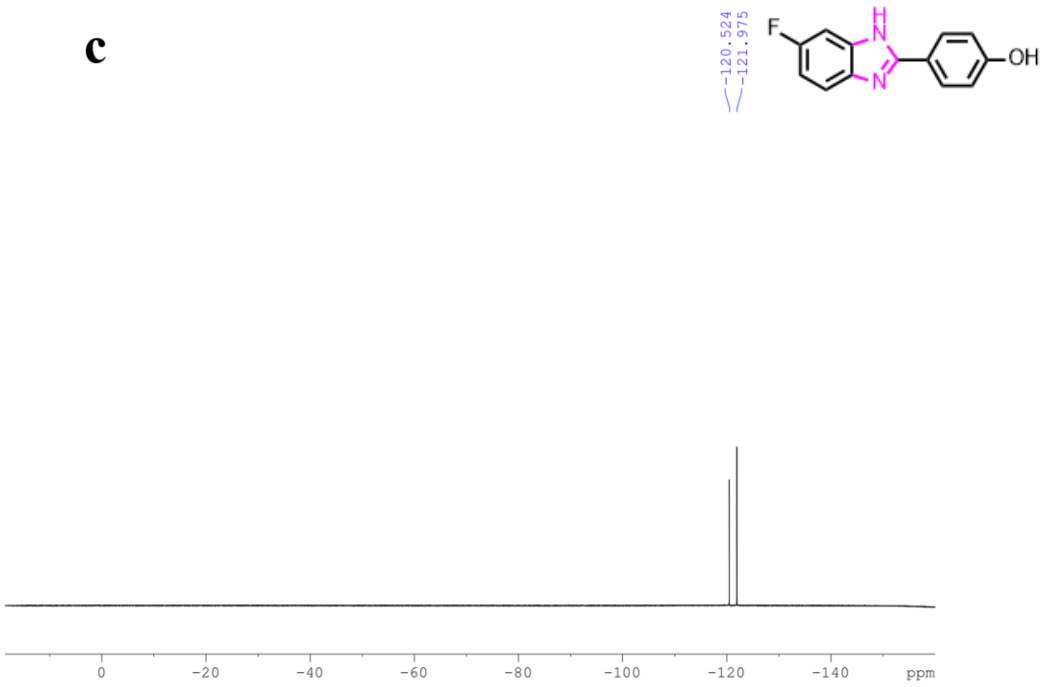
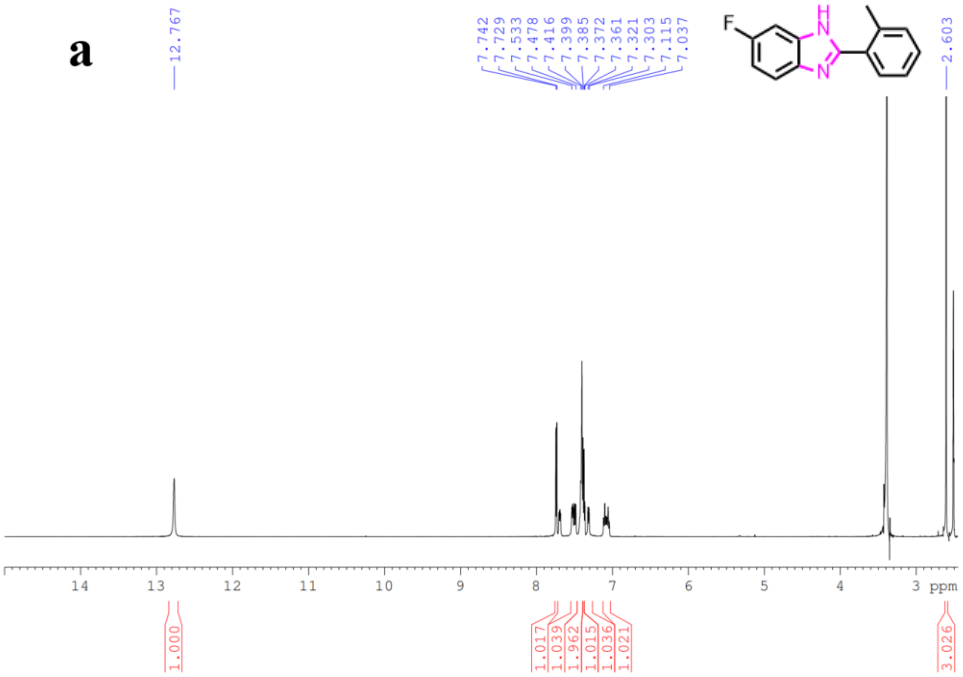


Figure S24. (a) ^{1}H NMR, (b) ^{13}C NMR, and (c) ^{19}F NMR spectra of **3i**.



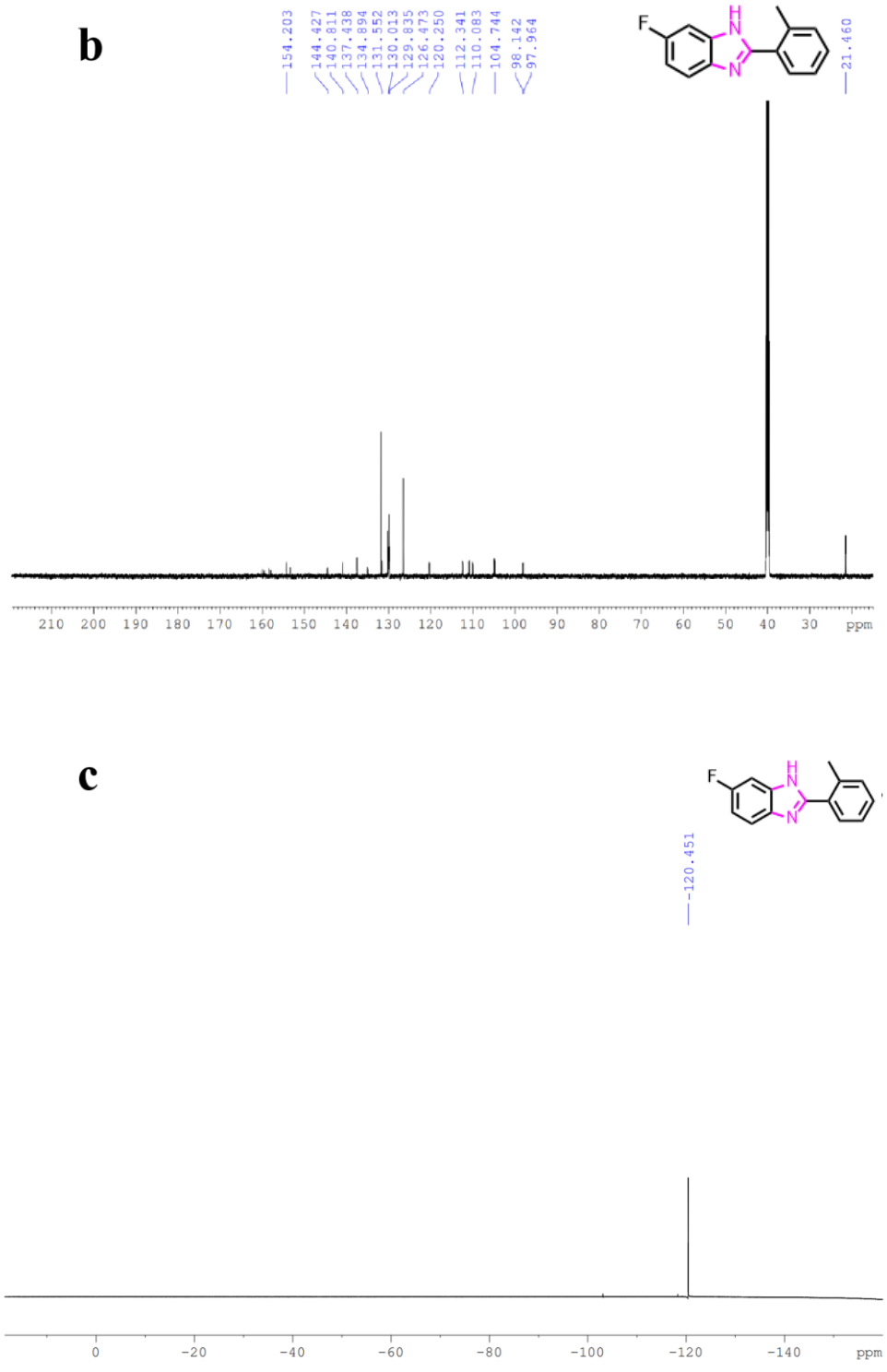
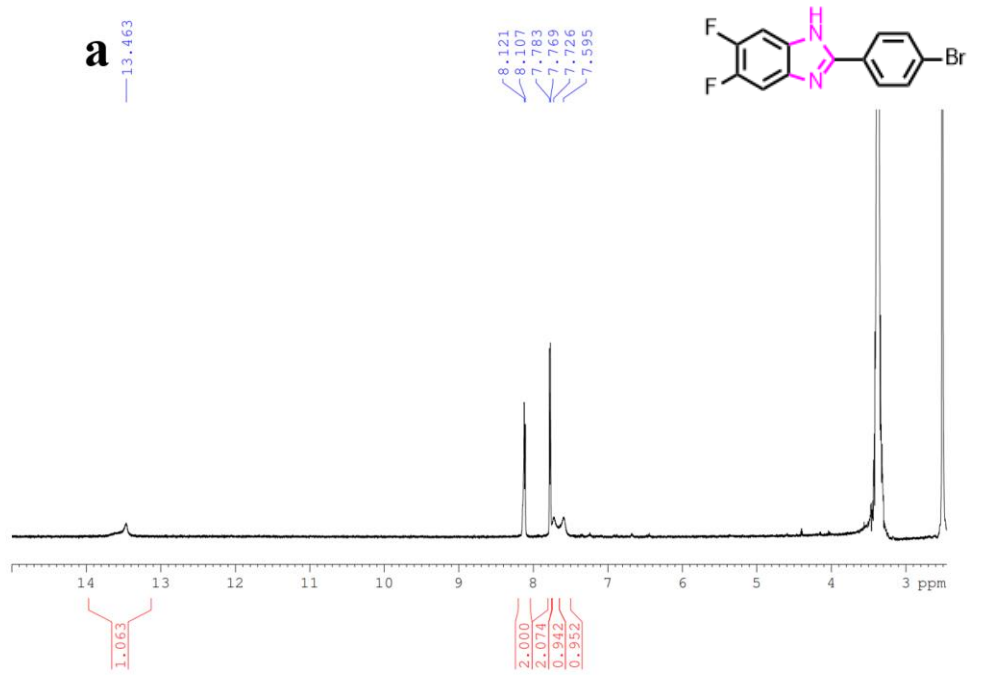
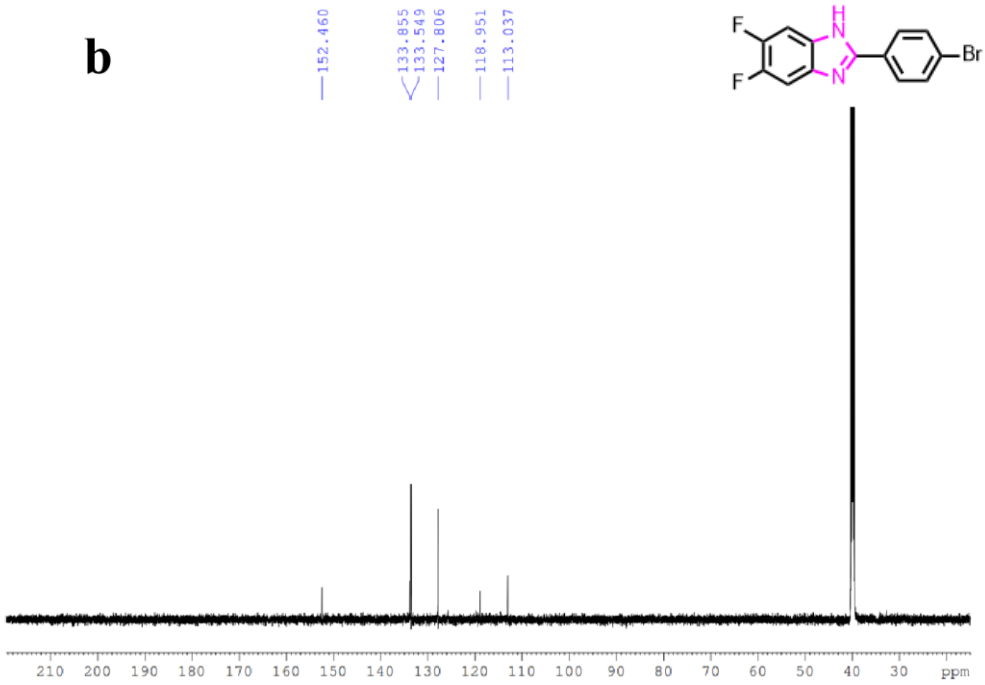


Figure S25. (a) ^{1}H NMR, (b) ^{13}C NMR, and (c) ^{19}F NMR spectra of **3j**.


a
13.463
8.121
8.107
7.783
7.769
7.726
7.595
F
F
N
H
N
Br
14
13
12
11
10
9
8
7
6
5
4
3 ppm
1.063
2.000
2.074
0.942
0.952


b
152.460
133.855
133.549
127.806
118.951
113.037
F
F
N
H
N
Br
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

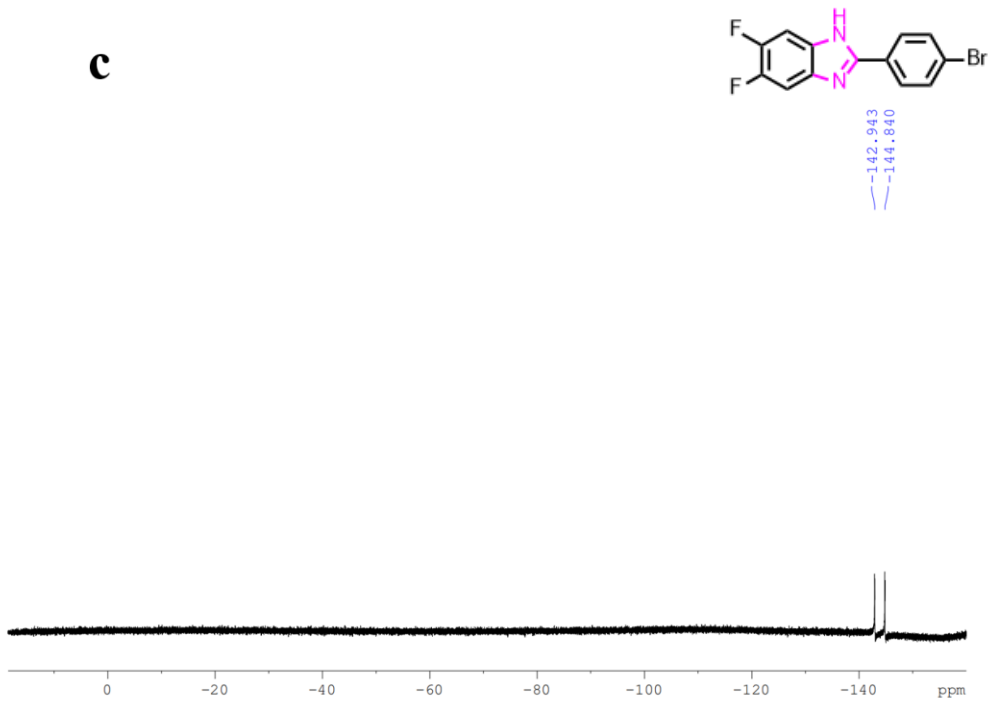
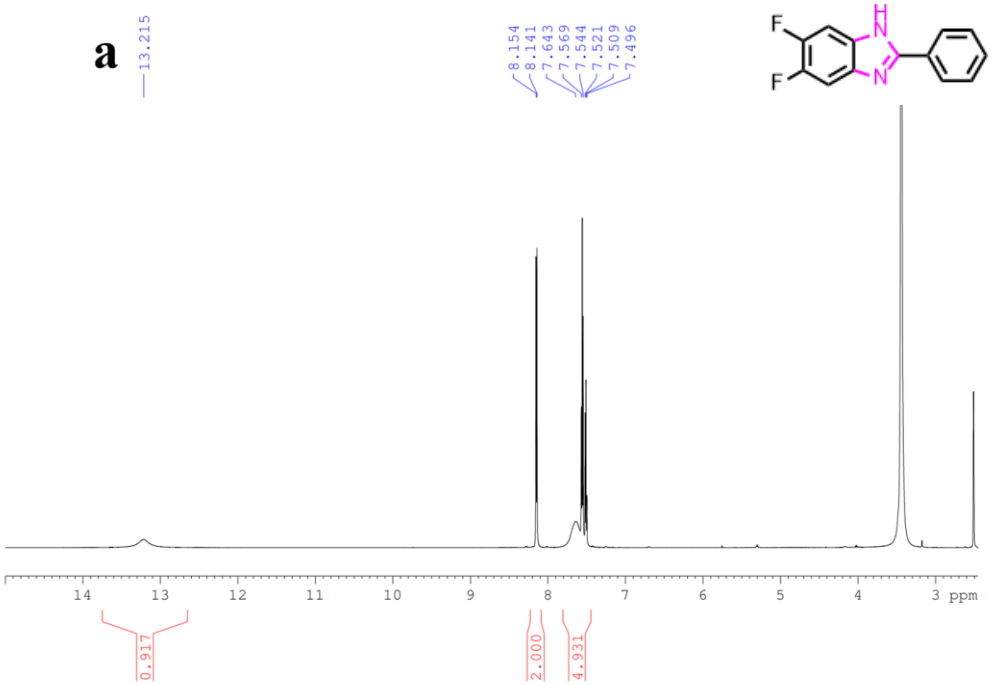


Figure S26. (a) ^{1}H NMR, (b) ^{13}C NMR, and (c) ^{19}F NMR spectra of **3k**.



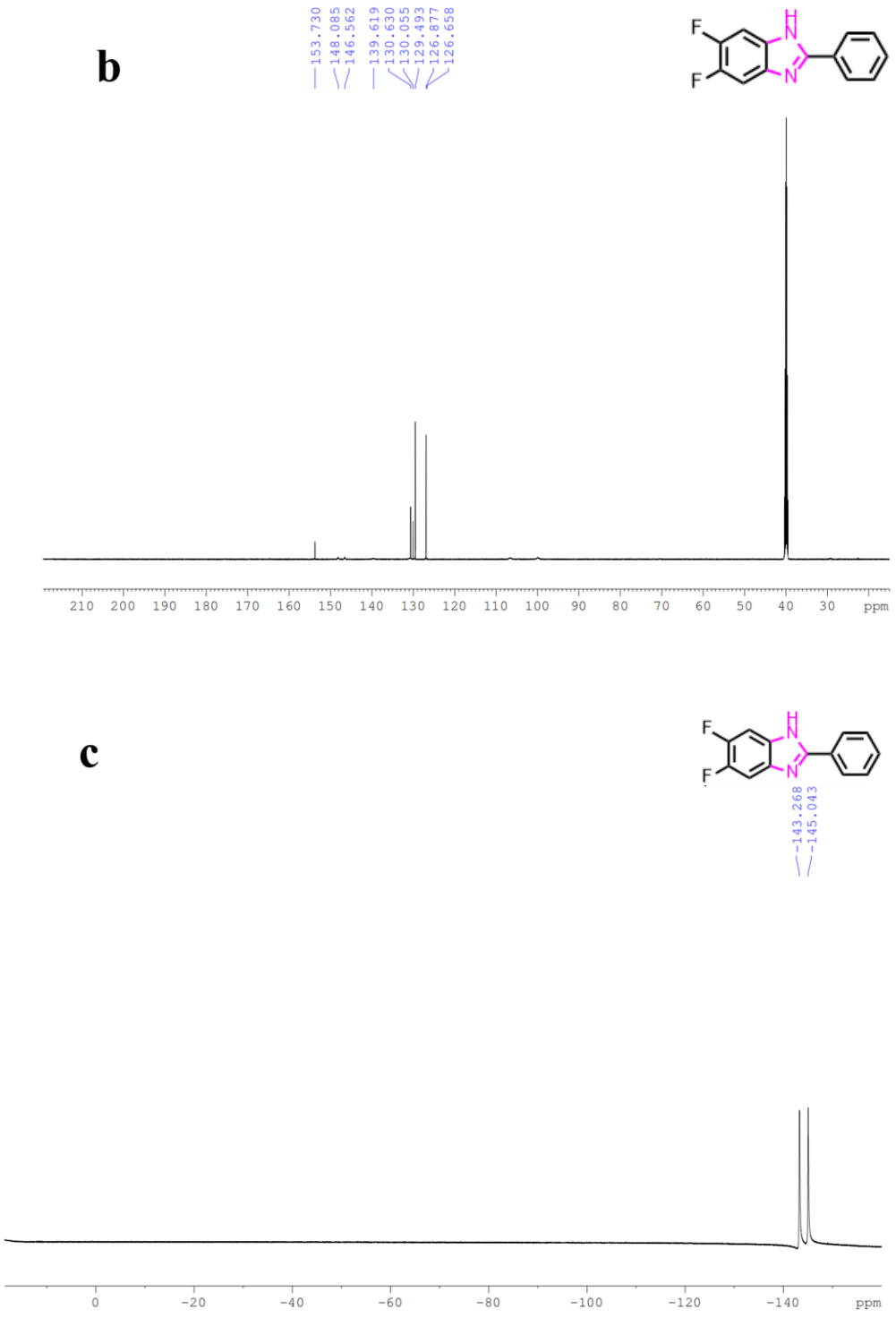
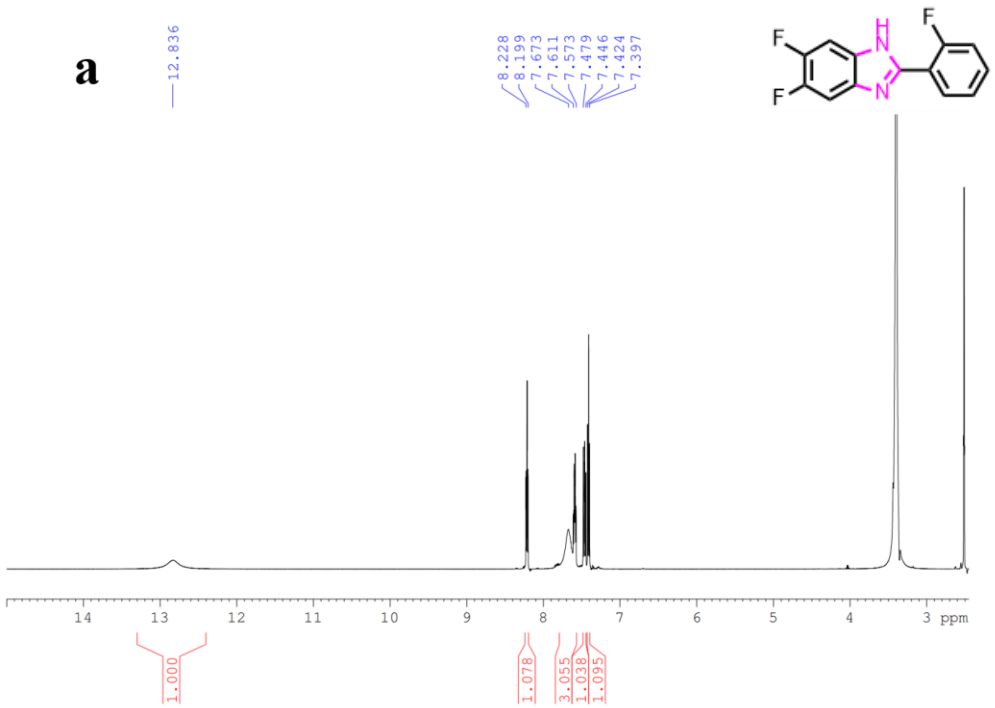
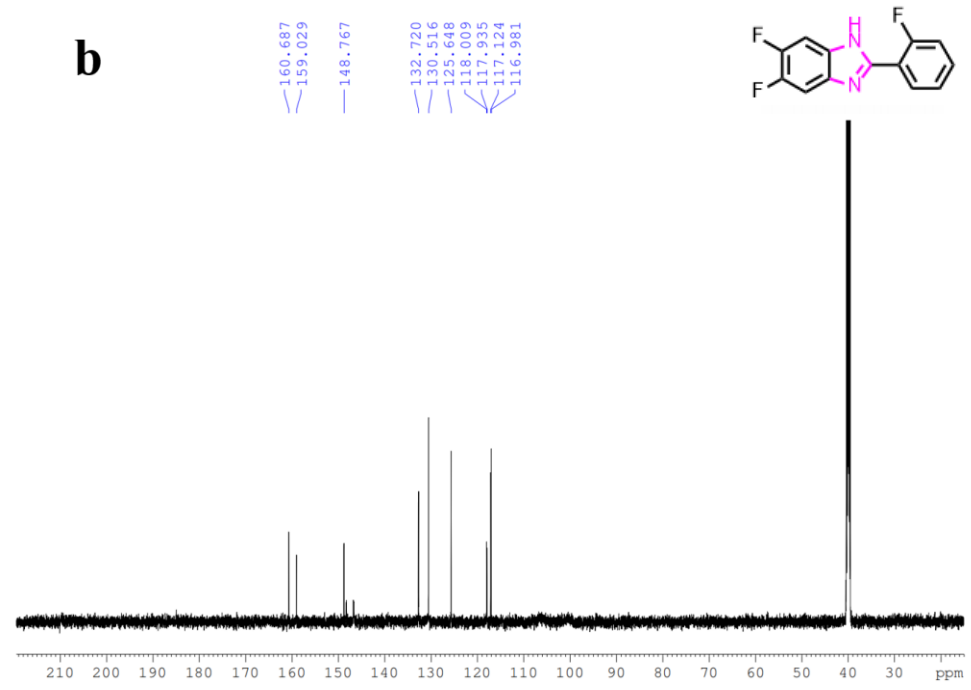


Figure S27. (a) ^{1}H NMR, (b) ^{13}C NMR, and (c) ^{19}F NMR spectra of **3l**.


a
12.836
8.228
8.199
7.673
7.611
7.573
7.479
7.446
7.424
7.397
F
F
F
N
H
14
13
12
11
10
9
8
7
6
5
4
3 ppm
1.000
1.078
3.055
1.038
1.095


b
160.687
159.029
148.767
132.720
130.516
125.648
118.009
117.935
117.124
116.981
F
F
F
N
H
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

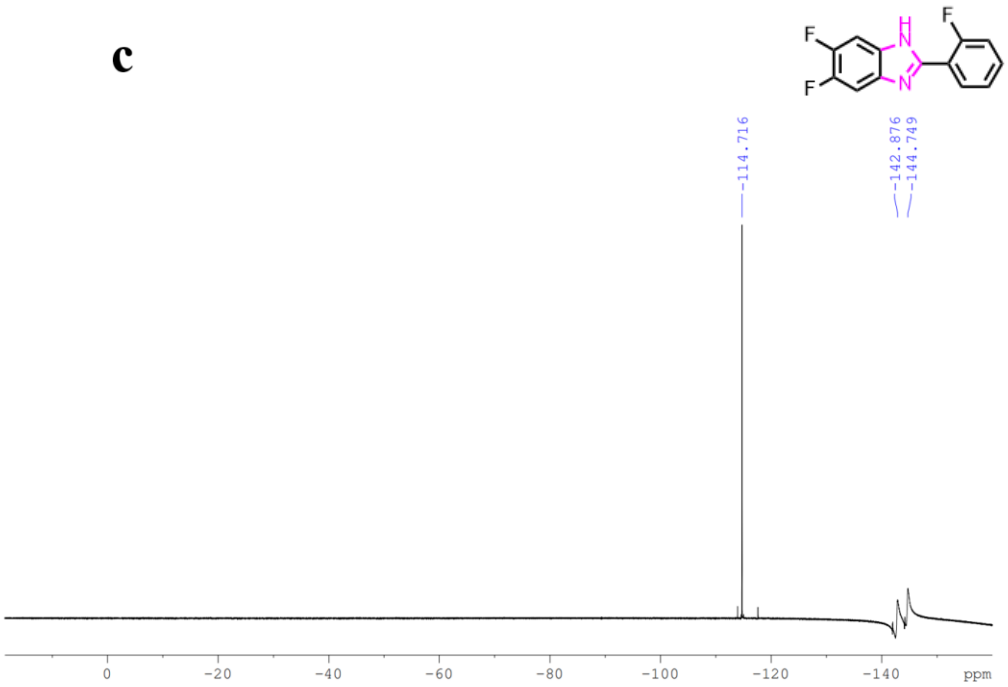
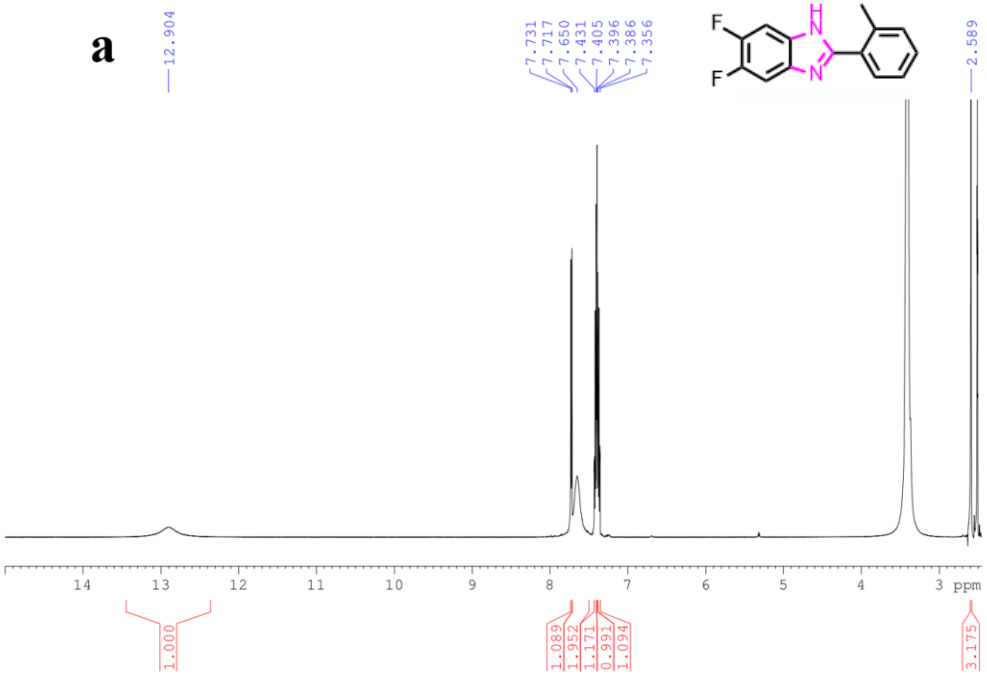


Figure S28. (a) ^{1}H NMR, (b) ^{13}C NMR, and (c) ^{19}F NMR spectra of **3m**.



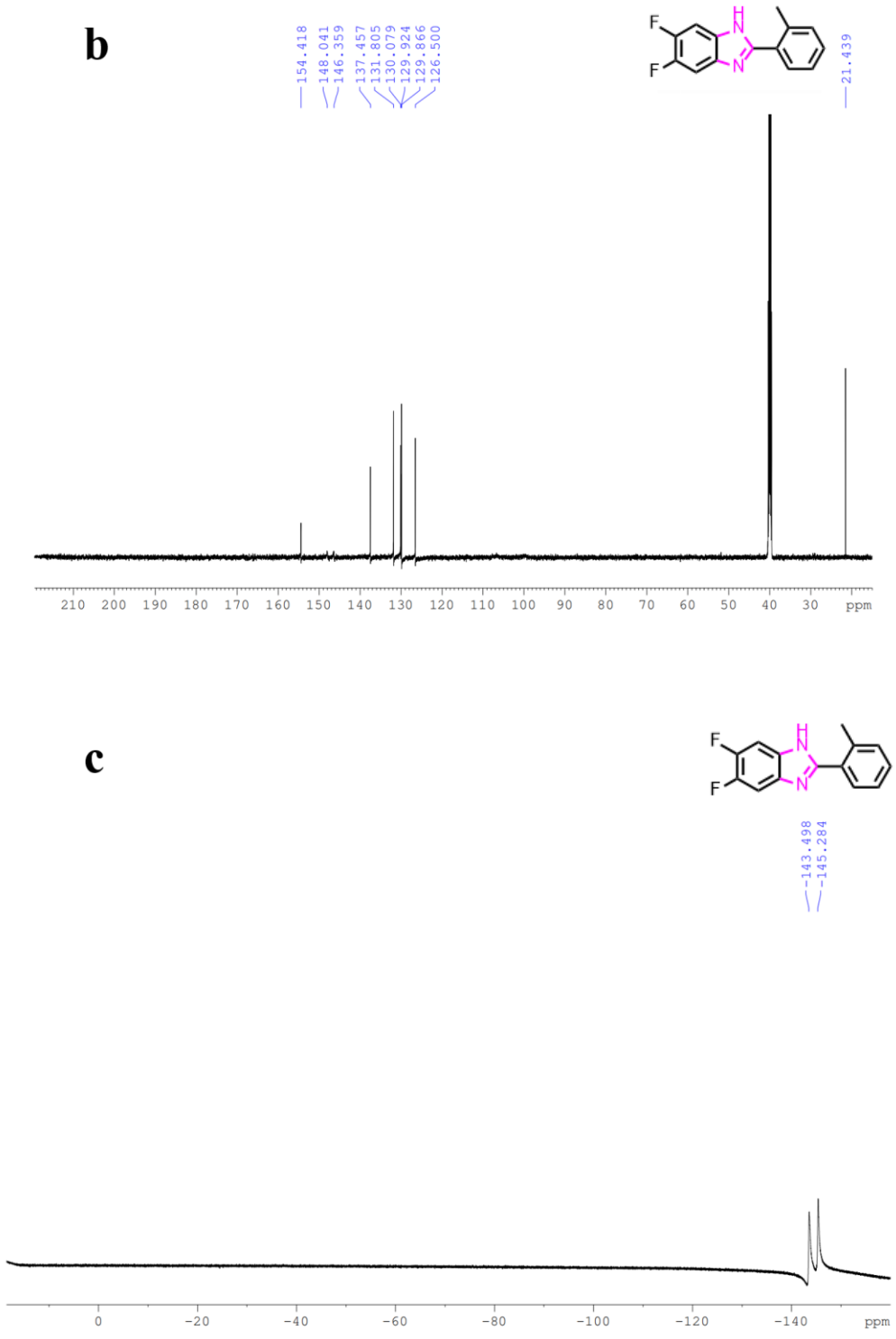


Figure S29. (a) ^{1}H NMR, (b) ^{13}C NMR, and (c) ^{19}F NMR spectra of **3n**.

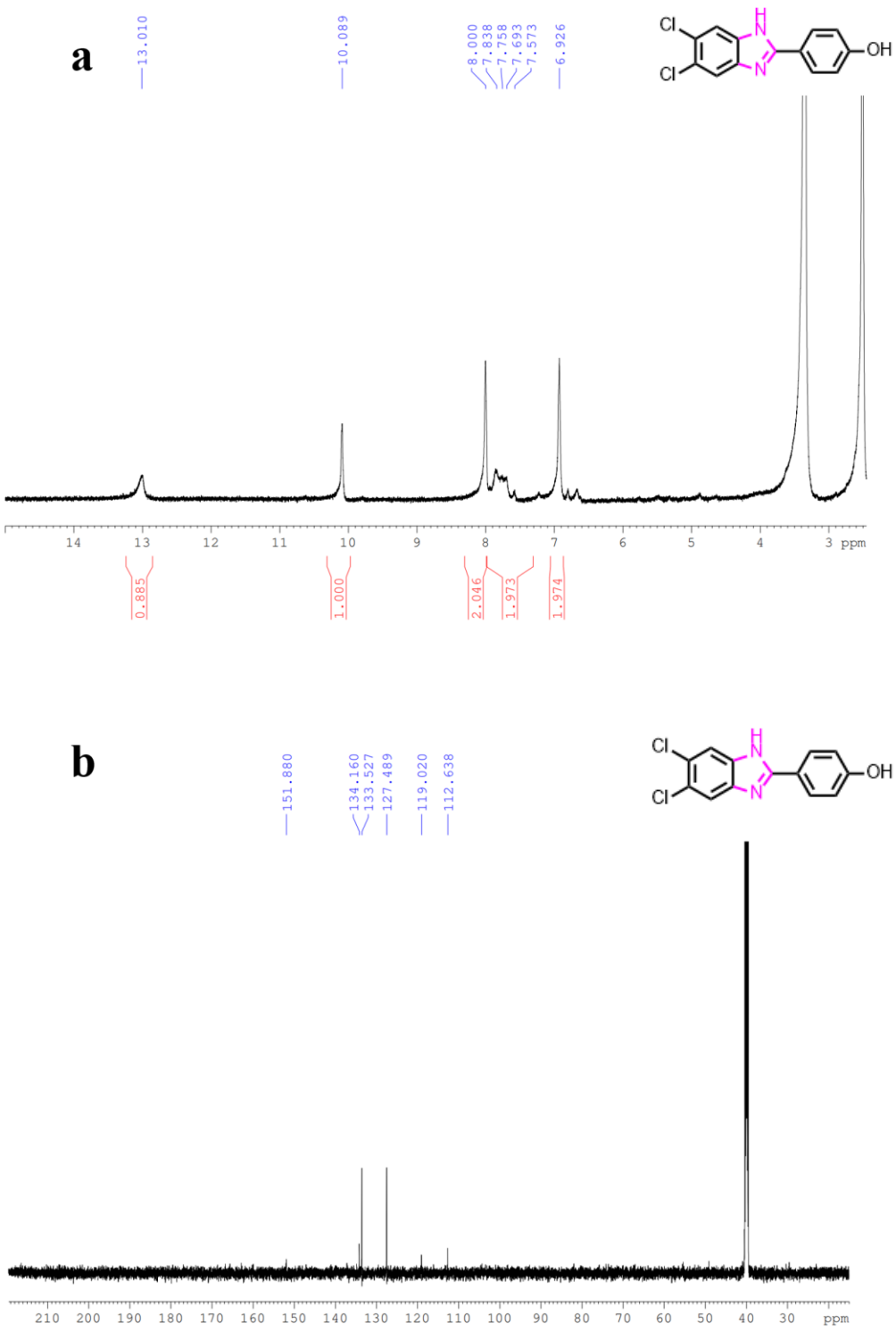


Figure S30. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of **3o**.

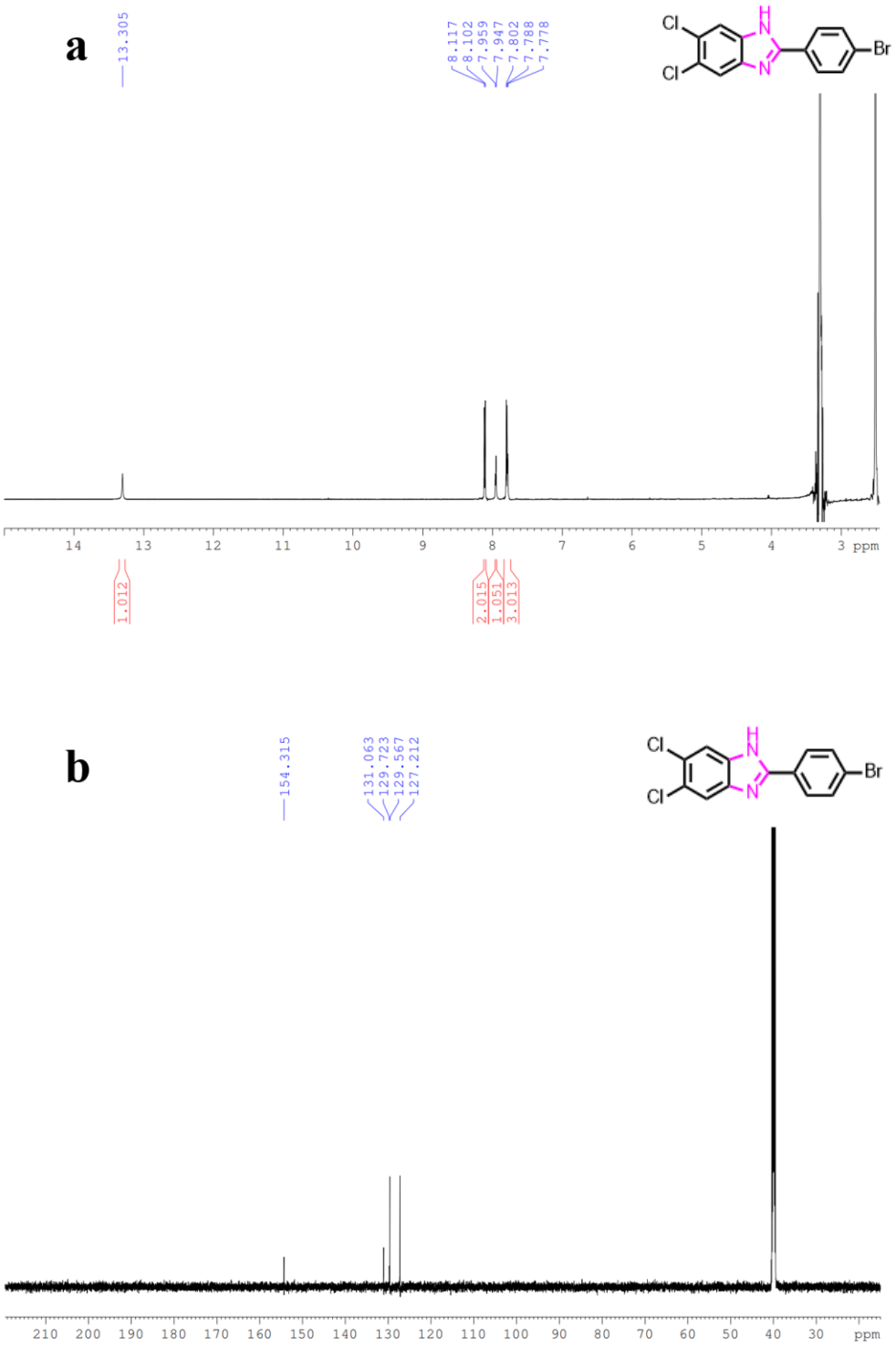


Figure S31. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of **3p**.

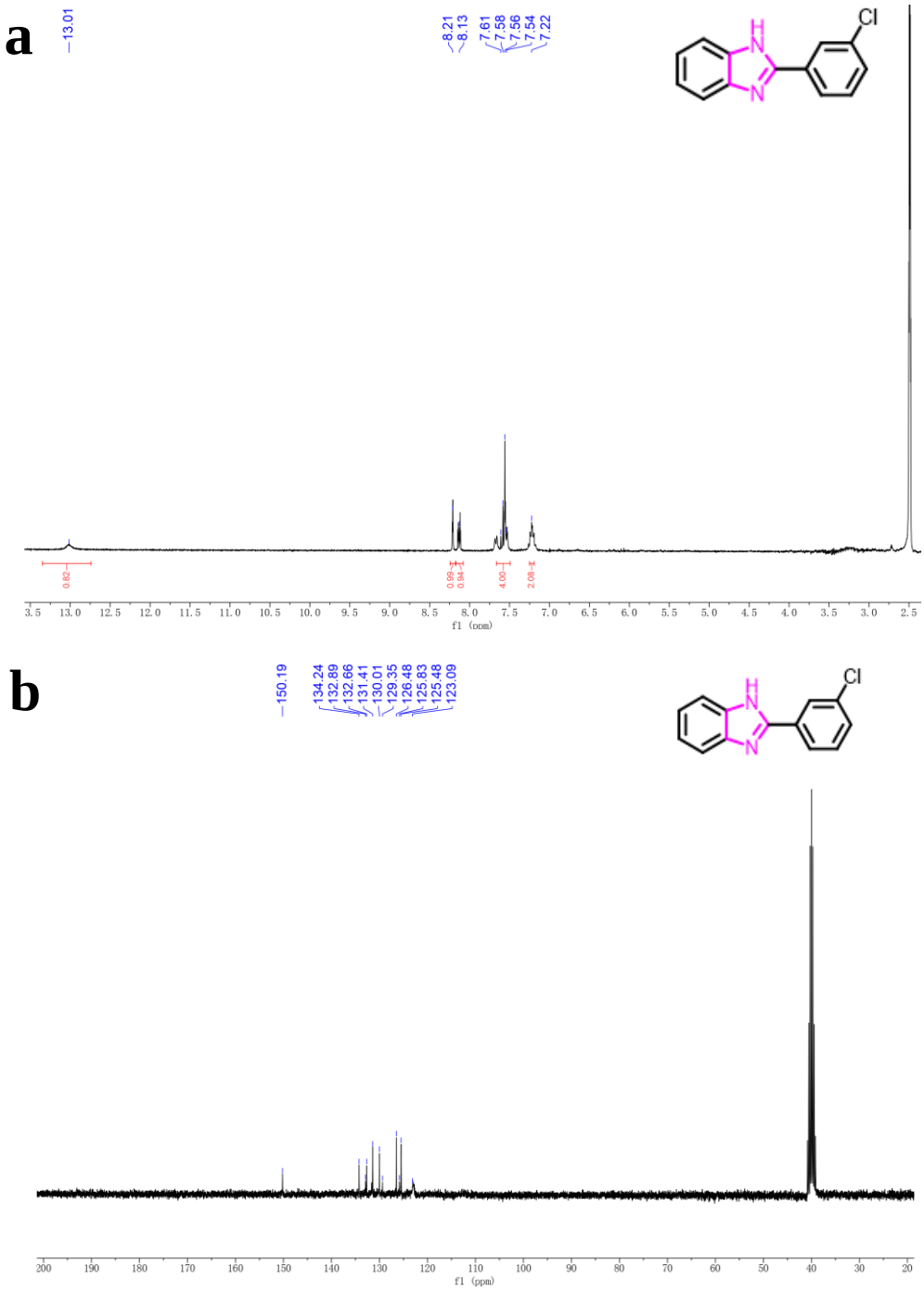


Figure S32. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of **3q**.

6. References

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